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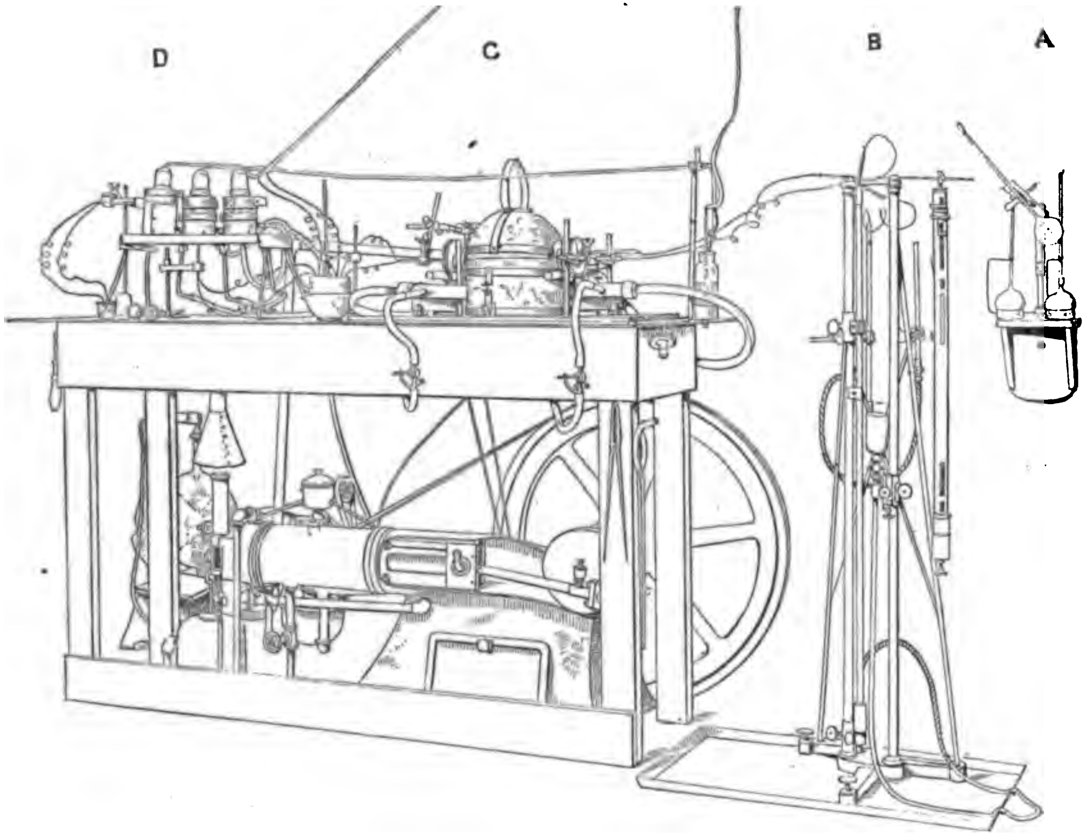

Frontispiece.—Disposition of apparatus for air thermometry and boiling-point. Scale $\frac{1}{20}$.

UNITED STATES GEOLOGICAL SURVEY
J. W. POWELL, DIRECTOR

ON THE THERMO-ELECTRIC MEASUREMENT OF HIGH TEMPERATURES

BY

CARL BARUS

WASHINGTON
GOVERNMENT PRINTING OFFICE
1889

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DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY,
DIVISION OF CHEMISTRY,
Washington, D. C., February 29, 1888.

SIR: I have the honor to transmit herewith the manuscript of Dr. Carl Barus's report "On the Thermo-electric Measurement of High Temperatures," and to request that it be published as a bulletin of the U. S. Geological Survey.

Very respectfully,

F. W. CLARKE,
Chief Chemist.

Hon. J. W. POWELL,
Director U. S. Geological Survey.

PREFACE.

The present publication is the first contribution to a research on the physical constants of rocks, the experiments of which are to follow a general plan devised by Mr. Clarence King, former Director of the U. S. Geological Survey. Retaining such questions as have an immediate bearing on dynamical geology for his own investigation, Mr. King honored me by placing the purely physical part of the inquiry into my hands. Our undertaking was begun some years ago. I was in communication with Mr. King as far back as the summer[1] of 1881, and much work in the way of determining the possibilities of the problems, of organizing methods of research, and of selecting and devising suitable apparatus, was done prior to 1882.

Not, however, until January of 1882 were definite steps taken toward the organization of a physical laboratory. The work in view was of too elaborate a nature to be undertaken by a single observer; and at my request Mr. King invited Dr. Vincent Strouhal, then of the University of Würzburg, to share my labors. Our early endeavors were of a pioneering kind. With the exception of a few instruments which had been used in the physical work in Nevada, and which came into our possession through the kindness of Mr. G. F. Becker, the early laboratory of the Survey was furnished entirely at the expense of Mr. King.

It is but just, in this place, to acknowledge a debt of gratitude which I in particular owe to Mr. Becker, by whom our efforts in the direction of physical research were befriended and advanced. It will be remembered that the first physical work on the Geological Survey was done under his direct supervision.[2]

The general scope of the problems to be undertaken, so far at least as their purely physical relations are concerned, has been briefly given in an article prepared under the direction of Mr. King, and printed by the Survey[3] for the year ending June 30, 1882. In this article I classified the parts of the proposed research as follows:

(*a*) Phenomena of fusion. These would comprehend temperature of fusion, specific volume at this temperature of the solid and of the liquid materials respectively, heat expansion, compressibility, latent heat of fusion, specific heats—all considered with especial reference to their variation with pressure.

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[1] Cf. Second Ann. Rept. U. S. Geol. Survey, 1882, p. 40.

[2] Cf. First Ann. Rept. U. S. Geol. Survey, 1880, p. 46; Second Ann. Rept. U. S. Geol. Survey, 1882, pp. 311, 319–330.

[3] Third Ann. Rept. U. S. Geol. Survey, 1883, pp. 3–9.

(*b*) Phenomena of elasticity and viscosity, considered, as before, with especial reference to their dependence on temperature and pressure.
(*c*) Phenomena of heat conductivity under analogous circumstances.

The article then proceeds to select the relation between melting point and pressure, as a problem the experimental difficulties of which are perhaps least formidable; as a problem, moreover, which for thermodynamic reasons may judiciously be decided upon as a point of departure. It develops certain general methods by aid of which increments of high melting point, however relatively small, are measurable even under conditions of very high pressure. It concludes by signaling the importance of special and preliminary researches on the measurement of high temperatures and of high pressures, with a view to the selection of such details of method as will best subserve the purposes in question.

Throughout the present research the points here mentioned have been carefully kept in mind. It is my judgment that few important steps in dynamical geology will be made until the methods for the accurate measurement of high temperatures and of high pressures have not only been perfected but rendered easily available. On the basis of this conviction the present memoir on high temperatures has been prepared; and though the experiments on temperatures may seem to have been pushed to some detail, I can not regard them either as profuse or as superfluously ambitious. Indeed, if the investigation be of any fullness, it is almost essential that the observer master the component parts of his research separately; and not until he has satisfactorily done this can he apply them conjointly. In work like the present, moreover, the value of the data can scarcely be determined except by the degree of uniformity of great numbers of results.

In June, 1882, Dr. Strouhal resigned his charge to take a professorship at the University of Prague. At my request Dr. William Hallock was appointed to fill the vacancy, and, being at the time associated with Dr. Strouhal in certain duties abroad, he was easily able to complete the work which the latter had been compelled to leave unfinished. Dr. Strouhal made the purchases of all the instruments we desired to buy in Germany, while Dr. Hallock, following my instructions, proceeded to purchase such apparatus as could best be obtained in France.

About this time the rooms which had been placed at my disposal by the American Museum at New York became temporarily unavailable. Moreover, as Dr. Hallock had joined me, more room than the museum afforded was desirable. After due deliberation we determined to rent a house in New Haven, Conn., and thither the laboratory was removed in November, 1882. Our reasons for selecting New Haven were, briefly, that a satisfactory house for practical laboratory purposes could be obtained more reasonably there than elsewhere; and that the city offered excellent library and other facilities for scientific work, such as can be met with only in the immediate vicinity of a large university. We have abundant cause to thank the gentlemen in charge of the scientific department of Yale College for many favors which they kindly extended to us.

The researches made in New Haven, in so far as they fall within the scope of the present volume, are recorded in Chapter I. The bulk of our New Haven work, however, was in organizing a working laboratory and determining the errors and the constants of the instruments, and solving other problems which do not command sufficient general interest to be chronicled. The high-temperature work prosecuted there was laid out on a large scale, and the practical management of it is largely due to Dr. Hallock. Following Deville and Troost, the plan was one in which large masses of substances are thermally operated upon. Undoubtedly these researches would have led to important results beyond those of Chapter I if there had been time to carry them consistently through to the end.

The work in New Haven was not satisfactorily completed. In July, 1883, with the appointment of Prof. F. W. Clarke as chief chemist of the Geological Survey, our laboratory became officially connected with the chemical laboratory. Conformably with the further decision of the Director, by which the divers laboratories of the Geological Survey were united in one central laboratory in Washington, it was again necessary to change our basis of operations, this time (in November, 1884) from New Haven to Washington. In the quarters assigned to us in the U. S. National Museum, temperature work on so large a scale as the New Haven work appeared impracticable, and it was therefore abandoned.

In the mean time Dr. Hallock had been placed in charge of a series of independent researches not connected with my work, and the experiments in hand were carried forward by myself to the point indicated in the present volume. Of course I owe much to the experience gained in our mutual efforts, detailed in Chapter I.

In the introductory pages I give a succinct account of the chief methods of pyrometry which have thus far been put to the test.

I was fortunate in being able to avail myself of the fine working library of the American Academy, and I owe much to the courtesy of Dr. Austin Holden, the librarian in charge.

The actual investigations, as contained in Chapters II, III, IV, and V, were adapted to the conditions prevailing at the National Museum. In place of the dangerous and cumbersome apparatus of the former laboratory, the endeavor is made to reduce all apparatus to the smallest dimensions compatible with reasonable accuracy of measurement.

Methods of calibration of this kind based upon known thermal data (boiling points) are developed in Chapter II.

I make in Chapter III a cursory survey of certain pyro-electric properties of the alloys of platinum. Curiously enough, the data of this chapter led to a striking result, inasmuch as it appears that the zero resistance $f(0)$, if the resistance at t° be $r=f(t)$), and the zero temperature coefficient $f'(0)/f(0)$, are related to each other by a law which during the stages of low percentage alloying is independent of the ingredients of the alloy, except in so far as they modify its electrical conductivity.

In Chapter IV I develop a method for the direct and expeditious comparison of the thermo-couple with the air thermometer. A comparison of the data of Chapters II and IV gives me a criterion of the accuracy with which the data in the region of high temperature are known. This indirect method of arriving at such data is not apparently as rigorous as their direct evaluation by means of the air thermometer; but the indirect method requires much smaller quantities of substance and may be conveniently extended to much higher temperatures. Taking all liabilities to error into consideration, its inferior accuracy is only apparent.

The results recorded in these chapters will lead directly to the comparison of the data to be obtained with porcelain air thermometers containing different gases, or one and the same gas in all states of tenuity. When methods to be indicated in the text are pursued these comparisons can be made with great accuracy, since the stem errors and the expansion errors practically vanish. It is upon such results that the rigorous validity of known high-temperature data must ultimately depend. From my results, moreover, it does not seem absolutely essential to glaze the bulbs within. It thus appears probable that bulbs can be made of fire-clay body by which the upper limit of *direct* temperature measurement (1,500°) may be materially increased.

Finally, I propose in Chapter V a new method of pyrometry based on the viscous behavior of gases. Using the results of the earlier chapters, I endeavor to investigate the law of variation of gaseous viscosity and temperature. Having found that the said variation takes place nearly as the two-thirds power of absolute temperature, I proceed to indicate divers methods of utilizing this principle for practical high temperature measurement. The results show, I think, that when the law of thermal variation of gaseous viscosity is rigorously known, Poiseuille-Meyer's equation applied to transpiration data will enable us to measure temperature absolutely, over a wider thermal range, and with a degree of precision and convenience unapproached by any known method.

With regard to the contents of the present volume it is but just to remark that the work in all its essential parts was done either by Dr. Hallock and myself, or by myself alone without other assistance. The original practical construction of nearly all new apparatus, the designing and drawing of instruments, the extremely laborious computations which a task like the present involves, are our own work. If, therefore, in the writing of the present memoir I have apparently placed superfluous stress on mechanical details, I offer in explanation the fact that the result of personal experiences is my subject. It is much to be regretted that the valuable researches of Messrs. Deville and Troost were not given to the world in more explicit form, for I have spent much time and pains in re-investigating and retesting methods and processes which, if more elaborate publications by these brilliant experimentalists were accessible, would not have been necessary.

In conclusion I wish to make some reference to the makers from whom such special apparatus and supplies as are described in this volume were obtained. Mr. William Grunow,[1] whose accomplishments as a mechanician are too well known to need characterizing here, made the fine parts of the apparatus for us; the cathetometer, the manometer stand, the micrometer and appurtenances, the revolving muffle, and other apparatus being from him. Those parts of the apparatus which are of fire-clay—the furnaces, crucibles, tubes, etc.—were obtained from Messrs. Hall & Sons.[2] I desire especially to commend the technical skill of these gentlemen, as well as the pains and patience which they spent in making difficult parts of the work. Capillary tubes of platinum and silver I succeeded in inducing the Malvern Platinum Works[3] to draw for me. As I do not know whether platinum capillary tubes have previously been made, I wish to call attention to the fact that inasmuch as they can be heated to any temperature they are useful for many other purposes besides those given in this volume. Apparatus of porcelain, viz., air-thermometer bulbs and stems, fire crucibles, tubes, etc., were furnished in superior quality from MM. Morlent Frères,[4] ancienne M. Gosse. This firm constructed the standard apparatus for Deville and Troost, and their artistic skill is unsurpassed. The porcelain of Bayeux used in their apparatus, besides being of the most refractory kind, has this additional advantage that its heat-expansion constants are known. Bulbs were also successfully made for me by the Royal Prussian Porcelain Works,[5] at Berlin. These works are the makers of Professor Rieth's and Professor Angler's bulbs. The Saxon Porcelain Works,[6] at Meissen, courteously placed duplicates of such bulbs as they had already made (Professor Braun's bulbs) at my disposal. The glass apparatus, boiling tubes in various open forms, were originally made for me by Messrs. Whitall, Tatum & Co.,[7] who have excellent facilities for annealing glass. Closed forms of boiling tube, as well as the reentrant air-thermometer bulb of glass, were constructed by Emil Greiner,[8] with his usual accuracy and skill.

CARL BARUS.

PHYSICAL LABORATORY, U. S. GEOLOGICAL SURVEY,
Washington, January, 1888.

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[1] William Grunow, observatory, West Point, N. Y.

[2] Hall & Sons, No. 69 Tonawanda street, Buffalo, N. Y.

[3] Malvern Platinum Works, Jas. Queen & Co., agents, Chestnut street, Philadelphia.

[4] Morlent Frères, No. 8 Rue Martel, Paris, France.

[5] Königlich Preussische Porzellan Manufactur, Berlin; M. Andersen, director.

[6] Königlich Sächsische Porzellan Manufactur, Meissen; F. K. Büttner, director.

[7] Whitall, Tatum & Co., Philadelphia, Pa.

[8] Emil Greiner, No. 63 Maiden Lane, New York.

SUPPLEMENTAL.

Let me here add, before passing on, that since this manuscript left my hands some additional work has been done in high-temperature thermometry. A form of standard air thermometer has been devised and is being made. A torsion galvanometer suitable for the measurement of thermo-electric powers, such as are here encountered, has also been constructed. To test the efficiency of this instrument I made a series of measurements on the variation of boiling points with pressure, using the re-entrant porcelain crucible and the closed boiling tube figured below (Chap. II, Figs. 14*a* and 11*a*). The results for mercury, sulphur, cadmium, zinc, and bismuth, covering an interval of some 1,500° C., are important, inasmuch as they indicate the probable truth of the principle of Groshans. (Pogg. Ann., vol. 78, 1849, p. 112.)

I will advert to the independent method of standardizing a non-in-glazed re-entrant porcelain air thermometer bulb, by thermal comparison with a re-entrant glass thermometer bulb of known constants. Such comparison is to be made above 300° to obviate all moisture and condensation errors, and either directly in the elliptic revolving muffle, or indirectly through the intervention of the same thermo-couple. The difficult estimation of the volume of the non-in-glazed bulb is thus superfluous.

Again, to insure union, the gradual sagging of a weighted porcelain stem, the lower end of which has been heated to the viscous condition before the oxyhydrogen blow-pipe, into the heated neck of a re-entrant in-glazed bulb on the revolving table, has suggested itself. Similarly, atmospheric pressure may be brought to bear externally on viscous parts of bulb or stem. (Cf., p. 175.)

Regarding literature, I may briefly refer to a recent critical work by C. H. Bolz (Die Pyrometer, etc., 70 pp., Berlin, J. Springer, 1888), and M. H. Le Chatelier has recently extended his valuable pyrometric researches in various directions.

C. B.

Boston, Sept. 1, 1889.

NOTE.—The thermo-dynamic reasons referred to on page 18 are briefly these: In the notation of Clausius (Wärme-theorie, 2d ed., I, Braunschweig, 1876, p. 172), the first and second laws together lead to the equivalent of James Thomson's equation: $dT/dp=T(\sigma-\tau)/Er'$; and the second law gives the equation $dr'/dT=c'-k'+r'/T$. Starting with these equations of fusion, I purposed to formulate the relation between melting point and pressure, $f(p, T)=0$, from direct experimental measurements, using the relation only within the pressure limits of the experiment. From this point it is difficult to proceed, for it is next necessary either to measure $\sigma-\tau$ as a function of pressure and temperature, or to measure the corresponding relation of r'. In addition to the above equations the more general relations

$$c=c_p-\frac{T}{E}\frac{d_pv}{dT}\frac{dp}{dT} \text{ and } c_v=c_p+\frac{T}{E}\left(\frac{d_pv}{dT}\right)^2\Big/\frac{d_Tv}{dp}$$

are available.

ON THE THERMO-ELECTRIC MEASUREMENT OF HIGH TEMPERATURES.

BY CARL BARUS.

INTRODUCTION.

GENERAL ACCOUNT OF METHODS OF PYROMETRY.

Earlier digests.—Some account of the literature of high temperatures, and particularly of the masterly labors of Messrs. Deville and Troost, being essential here, it was deemed expedient to give a brief but fairly full digest of all the methods devised and applied for high temperature measurement. To do this I made the customary use of the Fortschritte der Physik and of the Beiblätter of the Annalen der Physik, though in nearly all cases I have gone back to the original authors. Much assistance was received from earlier summaries, those of Pelouze,[1] Becquerel,[2] Weinhold,[3] Fischer,[4] Sir William Thomson,[5] Nichols,[6] Browne,[7] Lauth,[8] and Shaw,[9] all more or less complete and written with widely different ends in view. I must also refer to the reports (1881 and 1884) of the committee appointed by the British Association for the Advancement of Science to investigate the state of our knowledge of spectrum analysis.

I shall try to submit a tolerably full summary of what has been done, in most cases, however, giving no more than mere mention of the work of the individual observers. Nor shall I make many critical statements, for the cardinal difficulties surrounding divers processes described for

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[1] **Pelouze:** Traité complète des Pyromètres; Paris, 1829.

[2] **Becquerel:** Recherches sur la détermination des hautes temperatures, etc.; Ann. ch. et phys., vol. 68, 1863, p. 49.

[3] **Weinhold:** Pyrometrische Untersuchungen; Pogg. Ann., vol. 149, 1873, p. 186.

[4] **Fischer:** Ueber Thermometer und Pyrometer; Dingler's Jour., vol. 225, 1877, pp. 272, 463.

[5] **Thomson:** Heat, § 10; Encyclopædia Brit., 9th ed., vol. 11, 1880, p. 558.

[6] **Nichols:** Am. Jour. Sci., 3d series, vol. 22, 1881, p. 363.

[7] **Browne:** Pyrometers; Nature, vol. 30, 1884, p. 366.

[8] **Lauth:** Mesures pyrométriques à hautes temperatures; Bull. Soc. Ch., Paris, new series, vol. 46, 1886, p. 786.

[9] **Shaw:** Pyrometer; Encycl. Brit., 9th ed., vol. 20, 1886, p. 129.

temperature measurement so readily suggest themselves to the student of modern physics that special attention to them is superfluous, whereas criticism of more searching value calls for special experiments. Such experiments, except in a few cases, I have not had occasion to repeat.

Character of the measurements.—It is impossible to read the earlier memoirs on high temperature research without a feeling of uneasiness and disappointment. There is no lack of ingenious contrivances or of well-devised methods, but the results obtained are usually sadly at fault. In many cases no data for the absolute identification of the measurements made are discernible. In other cases not only do observers, using different methods, fail to reach accordant results, but it is not unusual to find even skilled observers using the same method with errors in results as high as 10 per cent. for the same fixed high temperature datum, the boiling point of zinc. To secure certain facilities of manipulation Deville and Troost, at the outset of their researches, used iodine vapor as a gas for thermal measurement. This step must be regarded as a misfortune to science, and one which retarded the progress of high-temperature research many years. After the tendency of the iodine molecule to dissociate had been suspected, and the relative imperviousness of porcelain as compared with platinum air-thermometer bulbs had been clearly pointed out, the values of the boiling point of zinc begin to increase from the exceptionally low values of Becquerel (884°), and to decrease from the exceptionally high values of Deville and Troost (1,040° C.) over a total range of temperature of about 150°, until the final results of these observers (932° and 942°, respectively) agree to about 10°. Curiously enough, however, Weinhold, an observer of great assiduity and some experience, having made himself master of high-temperature measurement by the air thermometer methods, endeavors to redetermine the value of the boiling point of zinc, and finds a value (1,035°) as high as the highest datum of Deville and Troost. Fortunately the subject has been rescued from this condition of vagueness by the recent vigorous work of Violle, the results of which agree well with the mean data of Becquerel and of Deville and Troost.

My chief object in giving this outline is to place before the reader the nature of the difficulties with which the problem of high temperature measurement is surrounded, and to indicate the diversity of the results reached even by the best of trained observers. Methods which in the hands of different investigators lead to data so widely different as the values just cited are not apt to inspire confidence. It is perhaps more for this reason than because of real difficulties of manipulation that the gas thermometer has been so little used as a standard of reference in high-temperature measurement. For the experimental operations are not necessarily more complex than those called for in some of the empiric methods of standardization—methods which have further burdened the unfortunate subject of high-temperature research with their own allotment of vagueness of principle and inaccuracy.

Classification of pyrometers.—Thermometers which depend essentially on the properties of the substance used for thermal measurement are called by Thomson[1] intrinsic thermoscopes. They may be either continuous or not. It is with such intrinsic thermoscopes that practical pyrometry must be conducted, although the data of the gas thermometer, as appears from the recent pyro-chemical researches of Langer and Meyer,[2] may safely be regarded as non-intrinsic and absolute, particularly in the region of high temperatures. Almost every thermal phenomenon has been utilized for temperature measurement, and the devices employed may be conveniently classified by aid of these phenomena as follows:

- I. Dilatation of solids.
    - 1. A single solid.
    - 2. Two solids acting differentially.
- II. Dilatation of liquids.
- III. Dilatation of gases.
    - 1. Expansion measured in volume, manometrically.
    - 2. Expansion measured in pressures, manometrically.
    - 3. Expansion measured in volume, by displacement.
- IV. Vapor tension.
- V. Dissociation.
- VI. Fusion.
- VII. Ebullition.
- VIII. Specific heat.
- IX. Heat conduction.
- X. Heat radiation.
- XI. Viscosity.
    - 1. Of solids.
    - 2. Of liquids.
    - 3. Of gases.
- XII. Spectrophotometry and color. Rotary polarization.
- XIII. Acoustics (wave length).
- XIV. Thermo-electrics.
- XV. Electrical resistance.
- XVI. Magnetic moment.
- XVII. Miscellaneous.

Dilatation of solids.—Curiously enough the dilatation thermometers were not the first to suggest themselves. Newton, in his scala graduum caloris, proposes a method of temperature measurement based on his law of cooling, almost as early as 1700. However Musschenbroek (1731), Ellicot (1736), Bouger (1745), and others availed themselves of single-bar expansion devices, and Mortimer made a thermometer on this principle in 1746.

The most celebrated apparatus of this kind (1782) is Wedgwood's[3] pyrometer, in which the attempt is made to express temperature in a scale based on the shrinkage experienced by a little compressed cylinder of clay after exposure to the said temperature. This apparatus came into much more general use than its inventor intended. Its indications were vigorously discussed by the physicists of the time, especially by Guyton-Morveau,[4] who in attempting to convert Wedgwood's arbitrary thermal scale into degrees centigrade showed the apparatus to be un-

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[1] Encyclopedia Brit., 9th ed., vol. 11, 1880, p. 580.

[2] Langer and Meyer, Pyrochemische Untersuchungen, Braunschweig, Vieweg u. Sohn, 1885; Berl. Ber., vol. 18, 1885, p. 1501.

[3] Wedgwood: Phil. Trans., Roy. Soc., vol. 72, 1784, p. 305; vol. 74, 1782, p. 358; Dingler's Jour., vol. 15, 1824, p. 230.

[4] Guyton-Morveau: Annales de chimie, Paris, 1st series, vol. 46, 1803, p. 276; ibid., vol. 73, 1810, p. 254; ibid., vol. 74, 1810, pp. 18, 129; ibid., vol. 90, 1814, pp. 113, 225.

reliable because of the tendency of clay to shrink irregularly and to warp, and because of its dependence on the kind of clay used and on the time of exposure. After this the use of single-solid pyrometers seems to have been abandoned until quite recently, when Mr. Nichols,[1] in comparing the resistance-temperature formulæ of Bénoit, Siemens, and Matthiessen with his own, found the linear dilatation of platinum very serviceable for the co-ordination of his data. He gives preference to the expansion thermometer over the resistance thermometer whenever the special constants of both instruments are unknown.

The absence of further devices for single-solid pyrometry is not remarkable when the vast numbers of pyrometers in which solids are combined differentially are taken into view. Some of the earliest attempts of this kind are due to Borda,[2] although Guyton-Morveau (loc. cit.) was probably the first observer who had pyrometric ends in view, the solids adopted being platinum and porcelain. This physicist was at some pains in systematizing the dilatation of solids. More elaborate attempts to utilize the occurrence of different expansibility in solids for pyrometric purposes are due to Daniell.[3] Daniell's substances are platinum and black lead, with a suitable interposition of clay, and his work on the dilatation of solids is elaborate, but unfortunately without much permanent value.

Following Daniell come a host of inventors whose apparatus, though often exceedingly ingenious, have only technical importance. These may therefore be passed over with a single brief mention here. Petersen[4] has a platinum wire in an iron tube; Gibbon[5] exposes rods of iron or steel, and copper provided with a contact lever; Oechsle[6] utilizes an iron-brass spiral working on the principle of Bréguet's metallic thermometer, while Clement[7] replaces the metals of such a spiral by platinum and silver. Prinsep,[8] however, held that even this apparatus is not reliable on account of the tendency of the metals to alloy—a conclusion which has Weinhold's[9] assent. Gauntlet,[10] Desbordes,[11] Oechsle,[12]

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[1] E. L. Nichols: Am. Jour. Sci., 3d series, vol. 22, 1881, p. 363.

[2] Borda: Boit Traité, I, 1816, p. 159. The use of iron and brass seems first to have been made by Felter in Braunschweig.

[3] Daniell: Experiments with a new register pyrometer for measuring the expansion of solids; Jour. Royal Soc., London, vol. 11, p. 309; Philos. Mag., London, 2d series, vol. 10, 1831, pp. 191, 268, 297, 350; ibid., 3d series, vol. 1, 1832, pp. 197, 261; Dingler's Jour., vol. 19, p. 416; vol. 43, p. 189; vol. 46, pp. 174, 241.

[4] Petersen: Gehler. Phys. Wörterb., 2d series, vol. 7, p. 994.

[5] Gibbon: Dingler's Jour., vol. 68, 1838, p. 436.

[6] Oechsle: Ibid., vol. 60, 1836, p. 191.

[7] Clement: Ibid., vol. 80, 1843, p. 241.

[8] Prinsep: Ibid., vol. 28, 1828, p. 421.

[9] Weinhold: Dingler's Jour., vol. 208, 1873, p. 125.

[10] Gauntlet: Ibid., vol. 157, 1860, p. 279.

[11] Desbordes: Ibid., vol. 157, 1860, p. 279.

[12] Oechsle: Ibid., vol. 160, 1861, p. 112; ibid., vol. 196, 1870, p. 218.

Bock,[1] Lion and Guichard[2] use iron and copper or iron and brass, either in the form of parallel rods or tubes bundled together or of a rod within a tube; in each case provided with a suitable index and dial arrangement. A like apparatus of metal and fire-clay (chamotte) is due to Bussius.[3] Finally, the use of graphite for pyrometry, an idea which long ago occurred to Daniell, was resuscitated by v. Steinle and Harting.[4] In their apparatus an iron tube surrounds a rod of graphite, and an ingenious mechanism permits only those parts which are actually exposed to the high temperature to act differentially on the dial. Adjustment is made by means of mercury. Winkler, who first tested these apparatus, declared them serviceable, but his testimony is not corroborated by Beckert. He finds that the indications of graphite pyrometers are neither strictly comparable nor very decisive, and that they are quite unreliable above 600°. This criticism applies to the pyrometers of the present class generally.

Dilatation of liquids.—Pyrometers based on liquid expansion are few in number and quite unavailable. An old apparatus is described anonymously in Dingler's Journal[5] in which the expansion of a fused alloy in a porcelain bulb is registered by aid of a platinum rod moving along a scale. The division is in Wedgwood degrees. A similar apparatus was proposed by Achard.[6] Here the expansion of the alloy is to be read off directly in the translucent stem of the porcelain bulb. The construction, therefore, is that of the ordinary mercury thermometer. I doubt whether either of these instruments has ever been used. Person[7] applied a new principle. He found that mercury under 4 atmospheres pressure boils above 450°, under 30 atmospheres pressure above 500°; that the dilatation in these cases is quite notable. Here I may refer to experiments of Byström,[8] to whom a hydro-pyrometer is due, and to Waterston,[9] by whom the expansion of water at high temperatures (300°) under pressure has been specially investigated. Waterston formulates his data and is led to the striking result that water at 300° expands at a greater rate than permanent gases. Water at high temperatures and pressures attacks glass, rendering it opaque and thus putting an end to the experiment.

Dilatation of gases (manometric methods).—According to Shaw[10] a rudimentary air thermometer was built by Amonton in Paris about as

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[1] Bock: Ibid., vol. 195, 1870, p. 312.

[2] Lion et Guichard: Ibid., vol. 220, 1876, p. 37.

[3] Bussius: Ibid., vol. 164, 1862, p. 107. Berg- und Hüttenm. Zeitung, No. 10, 1862.

[4] v. Steinle and Harting: Clemens Winkler's report in Zeitschr. für Analyt. Chem., vol. 19, 1880, p. 63; Beckert's report in ibid., vol. 21, 1882, p. 248.

[5] Dingler's Jour., vol. 32, 1829, p. 355.

[6] See Becquerel: Ann. ch., 3d series, vol. 78, 1863, p. 52.

[7] Person: Comptes Rendus, vol. 19, 1844, p. 757.

[8] Byström: Berl. Ber., 1862, p. 344.

[9] Waterston: Philos. Mag., Lond., 4th series, vol. 26, 1863, p. 116.

[10] Enc. Brit., vol. 20, 1886, p. 129.

early as 1700. Guyton-Morveau,[1] in whose thermal researches the dilatation of solids and the specific heat of platinum were discussed with reference to their availability in thermal measurements, also proposed gases for that purpose. Prinsep,[2] however, appears to have been the first to construct an air thermometer and to apply it as an instrument of research. Prinsep's bulb was of gold. This was in pneumatic connection with a reservoir of olive-oil provided with a sensitive manometer. As the air in the bulb expanded it displaced the oil which exuded through a cock at the bottom of the reservoir. Pressure being maintained constant the amount of olive-oil discharged is equal in bulk to the amount of air which enters the receiver at the given temperature. Hence by weighing the oil the temperature of the bulb may be calculated. Prinsep's apparatus is unique, and his absolute thermal data are very much nearer the truth than those of his predecessors. Indeed they compare well with the known data of the present day. Prinsep's chief data refer to the melting points of alloys of gold, silver, and platinum which bear his name. To these I shall recur.

Leaving Davy,[3] who constructed an air thermometer in which the air expansion was weighed in mercury, and Mill[4] and Petersen,[5] to whom also forms of air thermometers are due, the next observer seems to be Pouillet.[6] Pouillet's researches are of prime importance. Having constructed a bulb of platinum, which enabled him to reach the highest temperatures, he then took the first definite steps in radiation-pyrometry by investigating the temperature at which solids glow, in calorimetric pyrometry by determining the specific heat of platinum between 0° and 1,200°, and in thermo-electric pyrometry by carefully calibrating a thermo-couple of iron and platinum. As these apparatus will be referred to again, I need only remark here that to Pouillet the form of constant pressure manometer is due very nearly as it is to be used in pyrometric work to-day. This apparatus was perfected by Regnault,[7] and afterwards accurately figured by Pouillet[8] himself. Some time after this Silbermann and Jacquelin[9] described a platinum air-thermometer, of variable capacity, operating like a constant volume thermometer, but it does not seem to have led to practical results. Erman and Herster,[10] in their endeavor to measure the amount of permanent ex-

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[1] Loc. cit.

[2] Prinsep: Philos. Trans. Roy. Soc. Lond., 1827. Ann. ch. et phys., 2d series, vol. 41, 1829, p. 247.

[3] Davy: Dingler's Jour., vol. 46, 1832, p. 249.

[4] Mill: Gehler's Physikal. Wörterbuch, 2d series, vol. 7, p. 997.

[5] Petersen: Ibid., pp. 998, 1004.

[6] Pouillet: Recherches sur les hautes températures et sur plusieurs phénomènes qui en dependent; Comptes Rendus, vol. 3, 1836, pp. 782–790.

[7] Regnault: Relation des Expériences, Paris, vol. 1, 1847, p. 168.

[8] Pouillet: Physique, vol. 1, 9th ed, 1853, p. 233.

[9] Silbermann et Jacquelin: Bull. Soc. d'Encouragement, 1853, p. 110; cf Becquerel, loc. cit.

[10] Erman and Herster: Pogg. Ann., vol. 97, 1856, p. 489.

pansion of cast-iron at high temperatures, availed themselves of bulbs of copper and of platinum for their thermal measurements. These were used much after the manner of vapor-density bulbs. The long capillary necks could be closed at the desired temperature by a faucet, and the temperature was then calculated from the amount of water which entered the cold bulb. These experiments form a natural transition to the earlier researches of Deville and Troost,[1] in which a splendid improvement in thermal measurements was made possible by the introduction of porcelain bulbs to replace those of metal and of glass. Deville and Troost here use Dumas's well-known method to evaluate both temperature and vapor density. In their search for a heavier thermal gas than air they select iodine vapor preferably to mercury, inasmuch as the metal is apt to condense on the colder parts of the bulb and in falling down upon the hot parts to cause fracture. Using this iodine thermometer, they find that cadmium and zinc boil at 860° and 1,040°, respectively. They also measure the coefficient of expansion of porcelain by noting the length of the necks of their bulbs at different (high) temperatures (0°, 860°, 1,000°). Having found these data they proceed to the measurement of vapor densities, with results which are not of interest here.

The high values for the boiling point of zinc thus obtained conflicted very seriously with certain measurements subsequently made by Becquerel.[2] This observer used a platinum-palladium thermo-couple, the indications of which had to be carefully referred to Pouillet's platinum air thermometer. In this way Becquerel found the boiling point of zinc at 932°, more than 100° below that of Deville and Troost, as well as reaching a similarly low boiling point for cadmium, 746°. In the same paper the method of determining a series of melting points of metals is described and the data are fully given, and several final sections are devoted to radiation pyrometry. As regards accuracy of measurement and varied character of results, this paper is one of the most important in the history of pyrometry. It is to be noticed that Becquerel was aware of the probable permeability of platinum to gases at high temperatures. Further mention will be made of this later.

These discordant results necessarily provoked considerable discussion between Becquerel[3] and Deville and Troost,[4] which temporarily resulted in favor of the former.

Deville and Troost naturally reject Becquerel's low values, and be-

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[1] Deville et Troost: Sur la densité de vapeur d'un certain nombre de matières minerales; C. R., vol. 45. 1857, p. 821 (C. F. Berl. Ber., 1857. p. 73); C. R., vol. 49, 1859, p. 239; Ann. ch. et phys., 3d series, vol. 58, 1860, p. 257.

[2] Becquerel: Recherches sur la determination des hautes temperatures. Ann. ch. et phys., 3d series, vol. 58, 1863, p. 49.

[3] Becquerel: C. R., vol. 57, 1863, p. 855; Inst., 1863, p. 369; C. R., vol. 57, pp. 902, 925; Inst., 1863, p 385.

[4] Deville et Troost: C. R., vol. 56, p. 977; Inst., 1863, p. 161; C. R., vol. 57, 1863, pp. 894, 935; Inst., 1863, p. 377; ibid., p. 897.

lieve them to be erroneous because of the permeability of platinum at high temperatures. In doing this they refer to researches of their own[1] on the porosity of metals. Becquerel's reply is of an experimental character. He continues his work on air-thermometer pyrometry, replacing the platinum bulb with bulbs of porcelain, and availing himself both of constant pressure and of constant volume methods of measurement. Curiously enough the results of these new determinations are even below the former values, the boiling points of zinc and of cadmium being at 891° and 720°, respectively, while for the former as low a value as 884° was found. Becquerel dwells upon the excellence of the Pouillet method for high temperatures. Deville and Troost nevertheless refuse to regard these new results of Becquerel's as conclusive. They insist upon the impossibility of deriving accurate data with a porous reservoir. They point out that the large difference between Becquerel's present and former results is in itself to be looked upon with suspicion. They finally assert, inasmuch as Becquerel's pyrometers were not in immediate contact with zinc vapor, but were exposed in a closed lateral tube which issued from the zinc retort, that the datum measured is not the boiling point of zinc but a temperature below it. They finally repeat their own experiments with the same values as before. Becquerel again endeavors to show that the permeability of platinum did not seriously influence his results. He shows that his own researches are made in a way calling for much less skilled manipulation than those of Deville and Troost; and he finally adds that Deville and Troost have made but a single measurement with air, and that the use of iodine vapor as a gas for thermal measurement is not immediately warranted. Becquerel states the reasons for considering his boiling-point apparatus sufficient, but agrees that a possible error may be the impurity of his zinc. With these remarks discussion ended, being left without a final issue; but it is well to state, in passing, that the results of subsequent observers, including Deville and Troost themselves, have proved beyond a doubt that the later inferences of Becquerel's were very nearly correct. Victor Meyer,[2] I believe, was the first to suggest the possible dissociation of the iodine molecule at high temperatures, a behavior which he had established for chlorine. Meyer's views were corroborated and variously interpreted by Crafts and Meier,[3] by V. Meyer himself,[4] Crafts,[5] Troost,[6] Berthelot,[7] and others.[8]

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[1] Deville and Troost: Porosité du platine. Rép. chim. appl., 1863, p. 326; sur la perméabilité du fer à haute température; C. R., vol. 57, 1863, p. 965.

[2] V. and C. Meyer: Berl. Ber., vol. 12, 1879, p. 1426.

[3] Crafts and Meier: C. R., vol. 90, 1880, p. 606; Berl. Ber., vol. 13, 1880, p. 851.

[4] V. Meyer: Berl. Ber., vol. 13, 1880, p. 391; ibid., 1880, p. 1010.

[5] Crafts: Ibid., 1880, p. 1316.

[6] Troost: C. R., vol. 91, 1880, p. 54.

[7] Berthelot: ibid., p. 77.

[8] Cf. Deering: Chem. News, London, vol. 40, 1879, p. 87.

In 1863 Deville and Troost[1] began the publication of another series of investigations on high temperatures and boiling points. They describe their new porcelain air-thermometer bulb, which is a hollow sphere of porcelain, glazed both within and without, with a short neck, to which a capillary fissureless porcelain stem is soldered with feldspar, and the oxyhydrogen blowpipe. They propose to discard iodine and to use air in its place, giving their apparatus a form nearly identical with Regnault's[2] normal air thermometer. They insist on the importance of spherical bulbs, and the air contained is dried at red heat by aid of a vacuum pump. All the zinc is carefully purified, and used in large quantities (charges of 17 kg.). It is but just to add here, to the great credit of Deville and Troost, that the actual construction of the porcelain air thermometer occupied them for nearly seven years, working in concert with M. Gosse, in charge of the porcelain works at Bayeux. They were the first to use metallic vapor baths for constant high temperatures, a method which has been adopted by Becquerel and by physicists generally since that time. In 1864 Deville and Troost[3] proceeded toward the accurate measurement of the heat expansion of the Bayeux porcelain. Using a porcelain bulb simultaneously and of the same material as the porcelain of the dilatation apparatus, they have the data sufficient to eliminate the error due to heat expansion from the thermal measurements made. Their method is necessarily one in which the linear expansion of a porcelain rod exposed in a zone of known constant temperature is measured by the cathetometer. Two platinum buttons, inserted in the ends of the stem, subserve the purpose of fiducial marks, and they are viewed through long lateral porcelain sight-tubes in the constant temperature apparatus. In this way they show that in some 200 measurements the cubical expansion of porcelain, between 0° and 1,500°, is 0.000016 to 0.000017. Above 1,500° it becomes rapidly larger. In addition to this normal heat expansion, porcelain experiences permanent dilatation, as is proved both by measuring the linear dimensions and by density tests applied to the porcelain after heating. Curiously enough, this density diminishes with frequent heating. The permanent expansion, which is a very serious error in the first heating (the volume of a bulb increasing from 281.3^{cc} to 285.6^{cc} in six heatings, for instance), fortunately, soon becomes negligible. Deville and Troost, at the end of their work, justly congratulate themselves on these results: "Nous conclurons que la porcelaine de Bayeux, matière absolument imperméable et encore rigide aux 1,500° * * * capable de se dilater jusque là d'une manière uniforme, sans qu'on ait à tenir compte de sa dilatation permanente si ce n'est au but des expériences." They again emphasize the excellence of soldering together, with feldspar in the oxyhydrogen flame, the accurately calibrated bulb and stem.

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[1] Deville and Troost, vol. 57, 1863, p. 897.

[2] Regnault: loc. cit., Pl. I, Figs. 7, et seq.

[3] Deville and Troost: C. R., vol. 59, 1864, p. 162.

After these publications Deville and Troost made no further important contributions to high temperature thermometry for five years. The subject occupied Regnault,[1] who proposed two methods. The first of these small flasks of iron or porcelain are partially charged with mercury, and closed above with a loosely-fitting valve or stopper. These are exposed at the temperature to be measured, and this is calculated from the weight of mercury left after cooling. The other method, being a displacement method, will be described below. Shortly after this a series of very painstaking attempts in the measurements of high temperatures were made by Schinz.[2] Curiously enough, these papers, which contain a series of experiments admirably correct in principle, are but little known. Schinz, after endeavoring in vain to utilize the principles of heat conduction in practical pyrometry, and after testing Regnault's displacement method with unfavorable results, applies the thermo-electric methods of Pouillet and of Becquerel. Schinz's air-thermometer bulb is a huge iron cylinder, from the center of one end of which an iron capillary tube passes to the manometric apparatus, while an iron tube for the insertion of the junction of the thermo-couple projects inward to the center of the figure through the other end of the cylinder bulb. In this respect Schinz's thermometer is unique, being the only form of re-entrant bulb hitherto devised. The great advantage of this form of bulb, which, quite independently of Schinz, has been perfected in my experiments, will be emphasized below (Chap. IV). Nitrogen is the thermal gas in Schinz's work, and the calibrations are carried as far as 1,000°. Giving him full credit for correctness of method and for the assiduity with which he endeavored to carry it out, Schinz's apparatus was doomed to fail because of its impractical clumsiness of construction, to say nothing of the permeability of iron at high temperatures. It is not possible to make much definite progress in the measurement of high temperatures with an apparatus which falls short of the conditions of facility and certainty of manipulation. I shall revert to these measurements. For the special conveniences of the investigating chemist, Berthelot[3] devised an apparatus intended to be compact and very sensitive, and provided with an easily adjustable empiric scale. His instrument is based on the expansion of air and graduated by boiling points. Another instrument by Zabel[4] is so adjusted as to ring an electric bell at any given temperature. It is perhaps expedient to advert in this connection to the thermometers of Weinhold[5] and of Crafts,[6] both of which are constructed on Jolly's[7] plan, but so adjusted that the conditions of constant volume are secured by the aid of

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[1] Regnault: Ann. ch. et phys., 3d series, vol. 63, 1861, p. 39.

[2] Schinz: Dingler's Jour., vol. 177, 1865, p. 85; ibid., vol. 179, 1866, p. 436.

[3] Berthelot: Ann. ch. et phys., 4th series, vol. 13, 1868, p. 144.

[4] Zabel: Dingler's Jour., vol. 195, 1870, p. 236.

[5] Weinhold: Pogg. Ann., vol. 149, 1873, p. 186.

[6] Crafts: Ann. de Chim. et de Phys., 5th series, vol. 14, 1878, p. 409,

[7] Jolly: Pogg. Ann., Jubelband, 1874, p. 82.

an electro-magnetic engine. The mechanism of Crafts' new thermometers appears to be particularly perfect in this respect. An air thermometer in which the pressure is directly measured manometrically is described by Codazza.[1] A rigorous investigation of the formula of the air thermometer, with a view toward the construction of an apparatus of exceptional delicacy, has lately been made by Grassi.[2] Finally, the possible condensation of gases on metallic air thermometers of very large internal surface has been incidentally discussed by Fuess.[3] Operating with bulb in form of a cylindrical ring, Fuess found that for a correct ice point the boiling point of water showed a value enormously high, which gradually decreased without reaching a normal value. His research is unfinished, however, and thus the full interpretation of these anomalous results is yet to be given.

After the earlier work of Deville and Troost and the papers of Schinz, the most important memoir on high temperature measurement was published by Weinhold.[4] Having discussed the important methods of empirical pyrometry, with reference to their availability for practical work or for research, Weinhold uses his air-thermometer for a redetermination of the boiling point of zinc. Unfortunately his high value, 1,035° at 71.89^{cm}, which is only a little below the erroneously large values of Deville and Troost, casts a slur over much of Weinhold's elaborate experimentation, and his criticism on the merits of Siemens' pyrometer, of calorimetric pyrometers, and of the dissociation pyrometers fail to obtain the consideration which they probably deserve. Weinhold's bulb is of Meissen porcelain and his instrument of measurement is a modified Jolly thermometer.

In this place it is well to call attention to certain experiments commenced at about this time by Amagat and others to test the correctness of Boyle's law at different temperatures and high pressures. The constants hitherto adopted in high temperature air thermometry for all temperatures and pressures indiscriminately were those investigated by Regnault[5] and by Magnus.[6] By Amagat,[7] Cailletet,[8] and others these researches were pushed to great nicety for pressures as high as

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[1] Codazza: Dingler's Jour., vol. 210, 1873, p. 255.

[2] Grassi: Rend. dell' Academia delli Scienze fisiche e math., vol. 24, pp. 16, 131, 1885. Beiblätter, vol. 10, 1886, p. 387.

[3] Fuess: Zeitschr. für Instrumentenk., vol. 5, 1885, p. 274.

[4] Weinhold: Osterprogramm der höh. Gewerbesch. zu Chemnitz, 1873; Pogg. Ann., vol. 149, 1873, p. 186.

[5] Regnault: Relation des expèriences, Paris, 1847, pp. 15, 168.

[6] Magnus: Pogg. Ann., vol. 55, 1842, p. 1.

[7] Amagat: Fortschr. d. Phys., 1869, p. 155; C. R., vol. 71, 1870, p. 67; C. R., vol. 73, 1871, p. 183; Archives sci., phys. et nat. Genève, 2d series, vol. 40, 1871, p. 320; Ann. ch. et Phys., 4th series, vol. 29, 1873, p. 246; ibid., 5th series, vol. 22, 1881, p. 353, etc.; C. R., vol. 94, 1882, p. 847; C. R., vol. 95, 1882, p. 638; C. R., vol. 99, 1884, pp. 1017, 1153; C. R., vol. 103, 1886, p. 429.

[8] Cailletet: C. R., vol. 70, 1870, p. 1131.

500 atmospheres and for temperatures below 300°, and in the hands of Amagat they led to the discovery of minima of "pv." These researches, which must be passed over briefly here, are not as yet in a state of progress to enable the results to be at once applied. It is therefore reassuring to find in the labors of Langer and Meyer[1] a number of data tending to show that at high temperatures and for moderate pressures the constancy of the co-efficient of expansion of gases may be warrantably assumed.

To return from this digression to the subject in hand I find an important research by Erhard and Schertel[2] in which the melting points of Prinsep's alloys are again carefully determined by the porcelain air thermometer. The bulbs are of Meissen porcelain, and the method of measurement is essentially that of Weinhold. Finally, in 1880, Deville and Troost[3] publish a succinct account of their results in high temperature measurement, and thus conclude the interval of comparative silence.[4] They describe a new form of air thermometer, apparently superior to the Regnault normal form. In this instrument the air of the bulb is transferred into the measuring apparatus by a Sprengel's pump.

The bulb itself, being placed in a furnace fed by heavy petroleum oil, can be heated to any desired temperature by supplying a greater or smaller amount of fuel, through a graduated stop-cock. To eliminate the stem error they again use the "compensator," which is a closed porcelain capillary tube identical with the stem of the air thermometer and exposed side by side with it. This compensator is provided with its own manometric attachment. Nitrogen is used preferably to air.

The last memoir contains a full digest of their results on the boiling point of zinc. The methods of experiment and of measurement are also tersely given in chronological sequence. The authors put great stress on the purity of their zinc, on the fact that no iron was used in the retorts, on the great mass of zinc distilled (17 kg. to 20 kg.), on their methods of protecting their bulb from direct radiation by multiple screens, and on the great heat of the circumambient flame. The porcelain bulb, its peculiarities, and its construction are described with some detail. Their mean value for the boiling point of zinc, as Troost[5] subsequently remarks, is 942°, and the number of measurements made, 27. In some experiments made at a later date by Troost[6] the boiling point of selenium was found between 664° and 683°, the determination being feasible in a vessel of enameled iron. Troost[7] therefore concludes that

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[1] Langer u. Meyer: Pyrochemische Untersuchungen, 1885.

[2] Erhard and Schertel: Jahrbuch für das Berg-und-Hüttenwesen, im Königr. Sachsen, 1879, p. 154.

[3] Deville et Troost: C. R., vol. 90, 1880, pp. 727, 773.

[4] Deville: C. R., vol. 74, 1872, p. 145; is speculative, and refers to excessively high and to solar temperatures.

[5] Troost: C. R., vol. 94, 1882, p. 788.

[6] Troost: Ibid., p. 1508.

[7] Troost: Ibid., vol. 95, 1882, p. 30.

vapor densities in selenium vapor may safely be made in vessels of refractory glass, and recommends for that purpose the glass of Appert frères à Clichy, which is nearly rigid at this temperature. Other relevant results of Troost[1] on the permeability of platinum to hydrogen and of silver to oxygen at high temperature have been adverted to. Berthelot[2] points out the occurrence of unstable platinum hydrides. The value of the boiling point of zinc, to which the later researches of Deville and Troost had given a value compatible with that of Becquerel, was soon to be further fixed in position by the research of Violle.[3] Using a triple jacketed boiling point apparatus of enameled iron, he found by Deville and Troost's methods that zinc boils at 930°, thus giving further warrant to the data of Becquerel and Deville and Troost. In view of the accordance of these data, the problem of high temperature measurement may be regarded as solved with some accuracy as far as 1,500°. The greater share of the credit for this result is undoubtedly due to Deville and Troost, notwithstanding their unfortunate beginning and the fact that they allowed the subject to slumber in their hands for so many years. Violle refers to the problem of mere high temperature measurement as being one of great simplicity, and finds his main difficulty in the construction of constant temperature apparatus. My experience is the reverse of this. It is not very difficult to get the zinc point; but it is difficult to obtain thoroughly accordant values for it when *different* bulbs are used. Violle, who used but a single bulb (so far as I have been able to make out), obtains values which are almost identical, but which really apply only to the particular bulb in hand. The error possible in measuring the constants of the bulb is one of a very serious kind, and in case of a single bulb it remains arbitrarily fixed. The data of Deville and Troost, which were obtained by using a large assortment of bulbs, bear evidence to this. The differences between their later results are by no means insignificant, and these observers were most scrupulous in perfecting their methods, even to the fine points of experimental detail. Becquerel, in using divers thermometer bulbs, encountered the same wide limits of error. Regarding Becquerel's later and very low values, moreover, it is probable that the criticism of Deville and Troost applies. Becquerel's boiling-points apparatus was imperfect. In the case of so large an object as the air-thermometer bulb, at so high a temperature as the boiling point of zinc, its data can not be regarded as identical with the temperature of the vapor unless it be in actual contact with it. Evidence bearing on all these points will be repeated in Chapter IV.

Regarding Deville and Troost's experiments on the coefficient of expansion of porcelain, a short critical remark relative to the occurrence of permanent dilatation is in place here. When a porcelain rod is sus-

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[1] Troost: Ibid., vol. 98, 1884, p. 1427.

[2] Berthelot: Ann. ch. et phys., 5th series, vol. 30, 1883, p. 530.

[3] Violle: C. R., vol. 94, 1882, p. 720.

pended at one end and heated to extreme whiteness, it is probable that some permanent elongation will occur by virtue of the viscosity of the hot rod. The question therefore occurs whether this permanent expansion may not to some extent have produced the dilatation due to vitrification which they observed, or have been partially confounded with it. Messrs. Deville and Troost were careful to test the specific gravity of their heated porcelain, and they found a dimunition of density, a result in harmony with the dilatation observed. Again, the fact that permanent expansion vanished after successive heating in their experiments is evidence in their favor.

And yet I regard this remark not superfluous, because, in my own experiments, in which careful volumenometric tests of the volume of the bulb after successive heatings to 1,000° or 1,200° were made, I observed no permanent dilatation of volume. The increments I found would rather point to contraction. It does not seem probable, moreover, that porcelain which has been thoroughly fired in the manufacturer's furnace would continue to change in volume for some time after, at a temperature at which porcelain is appreciably viscous.

Dilatation of gases (*displacement methods*).—The next important step in air thermometry was made in Germany by V. Meyer and his pupils, although an ingenious suggestion, which was probably the main incentive to those researches, is due to the American, Crafts. So far as I have read, Regnault[1] appears to have been the originator of methods of air thermometry in which the thermal gas, instead of being measured manometrically, is chased out or displaced by a second gas, which can subsequently be absorbed or otherwise eliminated. Regnault's bulb is a large cylinder of iron provided with two capillary stems adjusted axially, and adapted for the admission and efflux of the gases. He bases his measurements on hydrogen, which is chased out, when the desired temperature is reached, by oxygen. Oxygen burns the hydrogen, and it is therefore necessary only to absorb and weigh the water thus produced. It is obvious that this operation may be repeated as often as is desirable.

Schinz (loc. cit.), who repeated these measurements, did not find them satisfactorily accurate. Nevertheless, a process which is of inferior accuracy below 1,500° may be very serviceable above the temperature at which the ordinary methods fail, and porcelain becomes viscous or even liquid. This appears to be the case with the displacement method as Crafts pointed out.

In 1878 Victor and C. Meyer[2] published an account of a new method of determining vapor density. In this the air contained was mechanically lifted or chased out at any given temperature by vapors issuing from the substance whose vapor density was to be determined. Inas-

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[1] Regnault: Ann. ch. et phys., 3d series, vol. 63, 1861, p. 39.

[2] V. Meyer: Berl. Ber., vol. 11, 1878, p. 1867; V. u. C. Meyer· Ibid., 1878, p. 2253; Dingler's Jour., vol. 231, 1878, p. 330; vol. 232, 1879, p. 418.

much as all these operations can be carried on under atmospheric pressure the apparatus was specially adapted for high temperature work. Messrs. Meyer[1], utilizing these advantages, were able to obtain definite evidence on the probable dissociation of chlorine and iodine vapor. Crafts and Meier[2] then pointed out that Meyer's method could very readily be adapted for temperature measurement. Optic, calorimetric, and electrical methods of temperature measurement, they contend, are all dependent on the air thermometer, the results of which are reliable only in the case of very perfect mechanism, and are not available above the temperature at which porcelain is rigid. By inserting a capillary platinum tube into the neck of Meyer's apparatus the air can be lifted out by a current of carbonic acid gas or of hydrochloric acid gas, both of which are easily absorbed. It is possible to make vapor density measurement to alternate with thermal measurements; and since the operation may be completed in two minutes, absolute rigidity of the porcelain vessel is not rigorously essential. Entering into the spirit of this suggestion, Meyer[3] and his pupils opened a new field of pyrochemical research, in which, after establishing the constancy of the coefficient of expansion of permanent gases at high temperatures, they extend their inquiries further to vapors. Meyer's apparatus here is a hollow sphere of porcelain provided with axial capillary tubes for influx and efflux of gas.

Following Meyer's summary, the linear character of the heat expansion of gases at high temperatures (barring dissociation) is to be regarded as established for selenium and tellurium (Deville and Troost), for nitrogen, oxygen, mercury vapor, and $As_2 O_3$ vapor (V. and C. Meyer), for hydrochloric acid, and carbonic acid gas (Crafts), and for hydrogen (Meyer and Züblin). These inferences antagonize the published opinion of Troost,[4] who, with Berthelot's acquiescence, prefers to regard the expansion of gases at high temperature (iodine for instance) as a physical function of temperature rather than to accept the occurrence of dissociation.

Meyer[5] and his pupils, however, push their investigations into much greater detail, adding to the number of gases of constant thermal coefficient and interpreting the variable behavior of others. Their new researches are carried on at temperatures even as high as 1,700°. Their apparatus is a long platinum tube provided with terminal capillary stems of platinum which have been ground into the somewhat narrower ends of the tube. This thermometric tube is surrounded by fire-clay which in its turn is enveloped by a second and wider platinum tube.

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[1] V. u. C. Meyer: Berl. Ber., vol. 12, 1879, p. 1426.

[2] Crafts and Meier: C. R., vol. 90, 1880, p. 606.

[3] Meyer: Berl. Ber., vol. 13, 1880, p. 2019; ibid., vol. 15, 1882, p. 1161.

[4] Troost: C. R., vol. 91, 1880, p. 54.

[5] Langer u. Meyer: Pyrochemische Untersuchungen, Braunschweig, Vieweg u. Sohn, 1885; Berl. Ber., vol. 18, 1885, p. 1501.

To obtain the high temperatures in question retort carbon is burned in an air-blast. The displacement method shows that oxygen, nitrogen, sulphurous acid, and even carbonic dioxide are stable at 1,700°. Platinum absorbs much oxygen and must be saturated with it before the thermal measurements are commenced. On the other hand, chlorine, bromine, iodine, carbonic oxide, steam, and even hydrochloric acid are more or less dissociated. Following these researches into further consequences, Meyer and his pupils[1] determine the vapor density of zinc, proving that all known metallic vapors are monatomic, and they even measure[2] the vapor densities of antimony, phosphorus, and arsenic, at 1,437°.

These brilliant researches contain the most advanced work thus far done on the subject of high temperatures, and it is upon the validity of some of their results, the non-dissociative character of the expansion of the permanent gases at high temperatures, that all high temperature thermal measurement depends.

Vapor tension.—Pyrometers of this kind have received little attention. Sajotschewsky[3] pointed out that the vapor tensions of different quantities of liquid are identical as far as the absolute boiling point, after which the curves diverge. He further studied the temperature and pressure relation of twelve liquids in detail, at least as far as the critical point. The importance of vapor tension thermometers was signalized by Sir William Thomson,[4] but the remarks refer principally to low temperatures. Shaw[5] has recently inquired somewhat rigorously into such pressure-temperature relations. For moderately high temperatures Crafts's[6] paper seems to be the only companion research to Sajotschewsky's. Crafts studied the boiling point and vapor tensions of mercury, and sulphur vapors, as well as of some carbon compounds with his hydrogen gas thermometer.

Dissociation.—The difficulty in the way of a successful application of vapor tension thermometers, Lamy believed to have been overcome in his dissociation thermometer. In the suppositive case of marble, for instance, originally placed in a vacuum, the pressure due to the evolution of carbonic dioxide will increase with temperature, and would finally revert to the pressure zero when the original temperature is again reached. Debray's[7] data for the dissociation of calcic carbonate and Isambert's[8] further researches on the gaseous dissociation of solids, suggest a number of materials. Lamy[9] incloses these in an exhausted

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[1] Mensching u. Meyer: Berl. Ber., vol. 19, 1886, p. 3295.

[2] Mensching u. Meyer: Gött. Nachr., 1887, p. 258.

[3] Sajotschewsky: Beiblätter, vol. 3, 1879, p. 741.

[4] Thomson: Proc. Royal Soc., Edinburgh, vol. 10, 1880, p. 532.

[5] Shaw: Trans. Cambridge Phil. Soc., Eng., vol. 14, 1885, p. 30.

[6] Crafts: Nature, vol. 26, 1882, p. 466.

[7] Debray: C. R., vol. 64, 1867, p. 603.

[8] Isambert: Thèse présente à la Faculté des sciences de Paris, 1868.

[9] Lamy: C. R., vol. 69, 1869, p. 347; vol. 70, 1870, p. 393. Dingler's Jour., vol. 194, 1869, p. 209; vol. 195, 1870, p. 525.

porcelain bulb. Weinhold (loc. cit.) who examined this apparatus condemns it, at least so far as the "pyromètre à marbre" is concerned. It appears that the carbon dioxide emitted is not again absorbed with sufficient regularity to subserve the purpose of thermal measurement. Perhaps Troost's[1] diffusion method for studying high temperature dissociation is to be added to this paragraph.

Fusion.—These pyrometers are discontinuous as well as intrinsic. Nevertheless, in virtue of their simplicity they are among the most serviceable of all the forms of pyrometers devised. As long ago as 1828, Prinsep,[2] using an air-thermometor bulb of gold, endeavored to measure the melting points of silver-gold, silver-platinum, and gold-platinum alloys. The brothers Appolt[3] investigated similar data for copper-tin alloys, using a calorimetric thermometer for high temperature measurement. A special double crucible for fusion of silver-platinum alloys is given by Heeren.[4] Temperatures estimated by alloy fusion were largely made use of by Plattner. Becquerel,[5] in his extended paper on the measurement of high temperatures, gave considerable attention to melting points. He used metallic wires and measured the fusing temperature with his calibrated thermo-couple. After him, Riemsdyk[6] made a series of measurements on metallic melting points. A very ingenious series of ring-shaped cups, placed on a common axis in a tier, was suggested by Heeren.[7] These cups contain rings of alloy, the consecutively varying melting points of which are stamped on the bottom of the cups. After each observation the rings are simply turned. Carnelley[8] made use of fusion pyrometers, substances of known melting points being inclosed in capillary tubes to serve for the identification of similarly exposed substances of unknown melting point. Results on the melting points of platinum alloys are due to Roberts.[9] A more elaborate series of researches is due to Violle,[10] whose data for high melting points are presumably the best in hand. Violle makes a careful study of the relation between specific heat and temperature. Assuming this relation to hold as far as the melting point in each case, he fixes this point for silver (954°), gold (1,035°), copper (1,054°), palladium (1,500°), platinum (1,775°), and iridium (1,950°), calorimetrically. For metals which melt below the platinum point, either the metal itself or platinum may be

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[1] Troost: C. R., vol. 89, 1879, p. 306.

[2] Prinsep: Trans. Royal Soc., London, 1827; Ann. ch. et phys., 2d series, vol. 41, 1829, p. 247; Pogg. Ann., vol. 13, 1828, p. 576; vol. 14, 1828, p. 529.

[3] Mitth. des Gewerbe Vereins für Hanover, 1855, p. 345.

[4] Heeren: Dingler's Jour., vol. 161, 1861, p. 105.

[5] Becquerel: Ann. ch. et phys., 3d. series, vol. 68, 1863, p. 49.

[6] Riemsdyk: Jahresber. d. Chem., 1869, p. 993; Chem. News, London, vol. 20, 1869, p. 32.

[7] Heeren: Zeitschr. des Vereins d. Ingenieure, 1876, p. 314.

[8] Carnelley: Jour. Chem. Soc., London, vol. 33, 1878, p. 281.

[9] Roberts: Ann. ch. et phys., 5th series, vol. 13, 1878, p. 111.

[10] Violle: C. R., vol. 85, 1877, p. 543; vol. 87, 1878, p. 981; vol. 89, 1879, p. 702.

made the basis of measurement. Both methods give the same result. The thermal comparisons are based on the porcelain air-thermometer of Deville and Troost. Furthermore, Erhard and Schertel[1] at about this time made elaborate re-determinations of the melting points of very pure Prinsep's and other precious alloys, by simultaneously exposing these alloys and a porcelain air-thermometer in a large muffle. Having obtained a series of silver-gold and gold-platinum alloys, melting between 984° and 1,408°, they apply these data practically, determining by means of them a table of melting points of known silicates (1,208° to 1,444°). Conechy,[2] at the suggestion of Carnelley, used fusing points to find the temperature at which arsenic volatilizes. Silicious mixtures of gradually increasing fusing points have been investigated by Seger, in Germany, and his tables are printed in full by Lauth,[3] who also gives some attention to alloy fusions. Seger's mixtures are made of feldspar, chalk, and kaolin, substances easily obtained, and they fuse between 1,100° and 1,700°. Finally, the data of Le Chatelier[4] must be mentioned, by whom fusing points, as well as temperatures of chemical decomposition, have been measured. Tables of melting points are published in great fullness by Carnelley.[5] Excellent and serviceable tables of this kind are also to be found in Landolt and Boernstein's[6] Physikalisch-chemische Tabellen.

Specific heat.—The measurements of temperature calorimetrically dates as far back as Guyton-Morveau,[7] in whose pyrometric researches it is definitely proposed. Schwarz[8] used both iron and water as well as platinum and mercury. Coulomb,[9] in studying the relation between hardness and permanent magnetization, determined the temperatures before quenching or annealing, by submerging the rods in water under known conditions. Clement and Desormes[10] use iron and water for technological temperature measurement, as was proposed also by others.[11] In general, however, neither is any attention given to the variation of specific heat and temperature, nor is allowance made for errors by radiation.

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[1] Erhard u. Schertel: Jahrbuch für das Berg u. Hütten-wesen im Königr. Sachsen, 1879, p. 154.

[2] Conechy: Chem. News, London, vol. 41, 1880, p. 189.

[3] Lauth: Bull. Soc. chim., Paris, vol. 46, 1886, p. 786.

[4] Le Chatelier: Ibid., vol. 47, 1887, p. 300.

[5] Thomas Carnelley: Melting and boiling point tables; London, Harrison & Sons, two vols., 1885.

[6] Landolt u. Börnstein: Physikalisch-chemische Tabellen, Berlin, Julius Springer, 1883.

[7] Guyton-Morveau: Ann. ch. et phys., vol. 46, 1803, p. 276; vol. 73, 1810, p. 254; vol. 74, 1810, pp. 18, 129; vol. 90, 1814, pp. 113, 225.

[8] Schwarz: Bull. Soc. Mulhause, 1827, p. 22; Pogg. Ann., vol. 14, 1828, p. 530.

[9] Coulomb: Pogg. Ann., vol. 14, 1828, p. 530.

[10] Clement and Desormes: Dingler's Jour., vol. 33, 1829, p. 145.

[11] Anonymous: Pogg. Ann. 2d series vol. 39, 1836, p. 518.

At this point Pouillet[1] took up these researches. He measured the specific heat of platinum between 0° and 1,200°, by direct comparisons with his platinum air-thermometer. The data found were so nearly constant as to give the calorimetric method of temperature measurement considerable importance. After a scientific basis had thus been given, the method was soon practically developed and many special forms of application were devised. Miller[2] describes an apparatus in which iron or platinum is quenched in mercury. This apparatus is discussed by Schubarth.[3] In an apparatus due to Wilson,[4] platinum or even clay is cooled in water. Schinz[5] recommends platinum and water. Siemens's[6] data are based on calorimetric measurements with copper and water. Bystrom[7] describes a platinum water pyrometer. Weinhold,[8] who reinvestigated the specific heat of platinum at high temperatures, found an anomalous behavior, while that of iron was quite regular. From these results for iron Schneider[9] calculated an extensive table. In view of the known anomalous behavior of iron at red heat, the regular variation of its specific heat, as compared with that of platinum, is certainly very remarkable, and quite at variance with more recent results of Pionchon (see below). Salleron's[10] pyrometer makes use of copper cooled in water. Special attention is to be given to Carnelley and Williams's[11] calorimetric work, in view of the many valuable data which these observers deduce by means of it. In their experiment a platinum vessel of special form is heated to the unknown temperature and then quenched in water. Fischer's[12] calorimeter again is adapted to furnace uses—cooling in water. Hobson[13] and, more thoroughly, Bradbury,[14] endeavored to apply a new method of calorimetric pyrometry. They cool the hot air of the blast with a known amount of cold air and measure the resulting temperature.

Thereupon Violle[15] began to publish the researches to which reference has already been made. By investigating formulated relations

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[1] Pouillet: C. R., vol. 3, 1836, p. 782.

[2] Miller: New Philos. Jour. Edinburgh, vol. 44, 1848, p. 126; Dingler's Jour., vol. 108, 1848; p. 115.

[3] Schubarth: Dingler's Jour., vol. 110, 1848, p. 32.

[4] Wilson: Philos. Mag., London, 4th series, vol. 4, 1852, p. 157; Dingler's Jour., vol. 158, 1860, p. 108.

[5] Schinz: Wärme-messkunst, 1858, p. 53.

[6] Siemens: Dingler's Jour., vol. 217, 1875, p. 291.

[7] Bystrom: Mechanics' Jour., 2d series, vol. 8, 1862, p. 15; Fortschritte d. physik, 1862, p. 244; ibid., 1863, p. 355.

[8] Weinhold: Pogg. Ann., vol. 149, 1873, p. 186.

[9] Schneider: Zeitschr. des Vereins Deutscher Ingen., 1875, p. 16.

[10] Salleron: Sci. Am., 1875, p. 50.

[11] Carnelley and Williams: Jour. Chem. Soc. London, vol. 1, 1876, p. 489.

[12] Fischer: Dingler's Jour., vol. 225, 1877, p. 467.

[13] Hobson: Ibid., vol. 222, 1876, p. 46.

[14] Bradbury: Ibid., vol. 223, 1877, p. 620.

[15] Violle: C. R., vol. 85, 1877, p. 543; Philos. Mag. Lond., 5th series, vol. 4, 1877, p. 318; C. R., vol. 87, 1878, p. 981; Ibid., vol. 89, 1879, p. 702.

between specific heat and temperature almost as far as 2,000°, he made silver, gold, copper, palladium, platinum, and perhaps iridium, available for thermal measurement. V. Meyer[1] before adopting Craft's suggestion had measured his temperatures calorimetrically. In America, practical calorimetric temperature measurement was studied with much success by Hoadley,[2] who describes an apparatus and the precautions to be observed. Like Violle, he endeavors to arrive at the melting point of platinum, and finds a small value of about 1,600 C. Mr. Hoadley, however, questions the purity of his platinum. An elaborate research published by Ehrhardt[3] proposes to find the specific heat of iodides, bromides, and chlorides throughout large ranges of temperature. Ehrhardt measures his temperatures with the porcelain air-thermometer and carries his investigations as far as 600°.

Finally, I desire to advert to an important research by Pionchon.[4] This observer makes a special study of the specific heat of iron between 0° and 1,000°, and finds a regular cubical formula to obtain between 0° and 655°. Between 660° and 723° the increase is much more rapid, and between 723° and 1,000° the relation is nearly linear. This interesting result adds a new anomaly to the behavior of iron at red heat, for in the last mentioned interval (723°–1,000°) the specific heat of iron is nearly double that which holds for the first interval.

Ebullition.—Reference to high temperature boiling points has already been made in the sections on air thermometry. Full data are given in the tables of Carnelley and of Landolt u. Bœrnstein, just mentioned. In this place I desire to call attention to the data of Crafts,[5] in which, by using napthaline and benzophenol, temperatures of ebullition between 140° and 350° are obtainable by the mere variation of pressure from 8.7^{cm} to 230^{cm}.

Heat conduction.—A simple device for a thermostat is made by Jourdes[6] who inserts a bar of metal into the furnace and measures the temperatures at points cold enough for the mercury thermometer. Heat is conveyed along the bar by conduction, and there are cavities to receive the thermometers. A somewhat different attempt of this kind is due to Main,[7] who surrounds a mercury thermometer bulb with asbestos and exposes it for stated lengths of time. Very elaborate attempts to determine the temperature on the inner surface of a furnace wall, by measuring the temperature of the outer surface under known conditions of conductivity, were published by Schinz.[8] Following a method origi-

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[1] Meyer: Berl. Ber., vol. 12, 1879, p. 1426.

[2] Hoadley: Jour. Franklin Inst., 3d series, vol. 84, 1882.

[3] Ehrhardt: Wied. Ann., vol. 24, 1885, p. 215.

[4] Pionchon: C. R., vol. 102, 1886, p. 1454.

[5] Crafts: Nature, vol. 26, 1882, p. 466.

[6] Jourdes: C. R., vol. 51, 1860, p. 68; Dingler's Jour., vol. 157, 1860, p. 151.

[7] Main: Ibid., vol 221, 1876, p. 117.

[8] Schinz: Dingler's Jour., vol. 163, 1862, p. 321; ibid, vol. 177, 1865, p. 85.

nally devised by Peclet,[1] Schinz first made a number of measurements of the heat conductivity of the material composing the furnace walls, devising special apparatus for that purpose. Having duly tested the method, however, he abandoned it because of the irregularity of the conduction phenomenon within the walls and because of its want of sensitiveness as compared with electric methods.

All the above methods have failed in practice. On the other hand, the circulating water-pyrometer due to Boulier[2] and others, in which the heat passing by conduction into the explorer or measuring part of the instrument is carried off by a current of water flowing between known levels, seems to be gaining in favor. The thermal estimate is made by measuring the temperature of the water before entering and after leaving the furnace. The indications are, of course, wholly empiric. In Boulier's compact and ingenious apparatus the explorer is a cylindrical box, with internal cylindrical partitions so adjusted as to secure a flow of water in cylindrical sheets. Water enters the outer compartment and leaves the inner, thus avoiding loss by radiation. According to Brown (loc. cit.) these apparatus, which are used with great success in connection with porcelain furnaces (Lauth), are due to Saintignon. Carnelley prefers a spiral explorer.

Radiation.—I have mentioned that the first temperature scale proposed was that of Newton[3] (1701) derived immediately from his law of cooling. A piece of red hot iron was experimented upon. Long after this M'Sweeney[4] proposed to catch the heat radiated from a furnace by a concave mirror, at the focus of which he placed a thermometer. Following close upon Govi's[5] photometric comparison of spectra, Becquerel[6] published his large memoir on high temperature pyrometry. Using the red copper glass, he investigates an exponential relation in which the photometric intensity of red light is expressed in terms of the temperature of the source of radiation. Green and blue glasses were also used. In addition to many results which must be omitted here, Becquerel proves that although all bodies have not the same power of radiation, truly opaque bodies like platinum, lime, magnesia, carbon, differ but little in this respect as far as the melting point of platinum. Oxdizable substances like iron and copper are not superficially opaque when covered by layers of oxide. Exterpolating by aid of his equation Becquerel finally concludes the 2,100° is probably the highest temperature electrically obtainable. The identity of emissive power accepted for

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[1] Peclet: Traité élément. de Physique, 4th ed., vol. 1, 1847, p. 418.

[2] C. F. Amagat: C. R., vol. 97, 1883, p. 1053; Lauth: Bull. Soc. chimique Paris, n. s., vol. 40, 1883, p. 108; Carnelley: Jour. Chem. Soc. London, vol. 45, 1884, p. 237; Lauth: Bull. Soc. chimique, Paris, vol. 46, 1886, p. 786, and others.

[3] Newton: Scala graduum caloris; Philos. Trans., vol. 22, 1701, p. 824.

[4] M'Sweeny: Pogg. Ann., vol. 14, 1828, p. 531.

[5] Govi: C. R., vol. 50, 1860, p. 156.

[6] Becquerel: C. R., vol. 55, 1862, p. 826; Ann. ch. et phys., 3d series, vol. 68, 1863, p. 49. Also Draper: Fundamental researches, Philos. Mag., vol. 30, 1847, p. 345.

opaque bodies by Becquerel,[1] involved him in a dispute with de la Provostaye[2] in which, however, the position of the former was not seriously impugned.

Decharme, repeating Pouillet's experiments, concludes that the intensity of the glow of metals, particularly of platinum, is largely dependent on the thickness of the wire. After this Crova[3] undertook a long series of experiments, in the course of which he made the subject of radiation pyrometry[4] practically his own. The law of emission being known, temperature may at once be measured spectro-photometrically. Crova in some of his experiments obtains his radiation directly from the bulb of a porcelain air thermometer. His results confirm Becquerel's datum that the emissive power of absolutely opaque bodies is the same. A series of experiments on radiation and temperature was published by Nichols,[5] who also uses his own results for a critical discussion of the work of Crova (l. c.) and of the indications of the radiation pyrometer in general. In the same year Stefan[6] published his law of radiation, according to which the amount of heat emitted by a hot body in vacuo increases as the fourth power of its absolute temperature. Violle,[7] using Gray's and Trannin's photometer, determined the photometric intensity of light emitted by glowing platinum at different temperatures, results which he endeavors to formulate. Similar experiments he subsequently makes for silver nearly at its melting point. An experiment with reference to temperature and incandescence was published by Bezold.[8] To put the law proposed by Stefan (l. c.) to a practical test, Schneebeli[9] commenced a series of experiments in which thermal measurements between 400° and 1,200° were made by a porcelain air thermometer of Schneebeli's[10] own construction. Radiation measurements are made by a crude bolometer[11] of tin foil, the instrument which Langley[12] has carried to a remarkable degree of perfection. Schnee-

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[1] Becquerel: C. R., vol. 57, 1863, p. 681; Annales chimie, 4th series, vol. 1, 1864, p. 120.

[2] De la Provostaye: C. R. vol. 57, 1863, p. 637; Ibid., p. 1022. The older papers of de la Provostaye et Dessains; see Ann.. de ch. et phys., 3d series, vol. 12, 1844, p. 129; Ibid., vol. 16, 1846, p. 337; ibid., vol. 22, 1848, p. 358; also de la Provostaye: Ibid., vol. 67, 1863, p. 1. Dulong and Petit's older radiation work is given in Ann. ch., 2d series, vol. 7, 1817, pp. 113, 225.

[3] Crova: C. R., vol. 87, 1878, pp. 322, 979; C. R., vol. 90, 1880, p. 252; Ann. chim. et phys., 5th series, vol. 19, 1880, p. 472; Jour. de phys., vol. 8, 1879, p. 196.

[4] Regarding spectrophometric work upon which measurement like the present largely depends, see Govi: C. R., vol. 50, 1860, p. 156; Trannin, Jour. de phys., Paris, vol. 5, 1876, p. 297; Vierordt: Pogg. Ann., vol. 1, 37, 1869, p. 200; Glan: Wied. Ann., vol. 1, 1877, p. 351.

[5] Nichols: Am. Jour. Sci., 3d series, vol. 18, 1879, p. 446; ibid., vol. 19, 1880, p. 42.

[6] Stefan: Wien. Ber., vol. 79, 2d series, 1879, p. 391.

[7] Violle: C. R., vol. 92, 1881, p. 866, 1204; C. R., vol. 96, 1883, p. 1033.

[8] Bezold: Wied. Ann., vol. 21, 1884, p. 175.

[9] Schneebeli: Wied. Ann., vol. 22, 1884, p. 430.

[10] Schneebeli: Arch. sci., phys. et nat., Geneva, vol. 8, 1882, p. 244.

[11] Svanberg: Pogg. Ann., vol. 84, 1851, p. 411.

[12] Langley: Am. Jour., 3d ser., vol. 21, 1881. p. 187.

beli finds that the law of Stefan very closely interprets his experiments. In a series of beautiful experiments Schleiermacher[1] puts the same law to a rigorous test. He heats a platinum wire to incandescence in an inclosure, the walls of which can be heated to different constant temperatures (0° to 200°), and from which all air has been carefully exhausted. The actual temperature of the wire is calculated from its resistance, a series of subsidiary researches in which the wire is compared with the porcelain air thermometer having previously been made. The amount of heat generated in the wire following from Joule's law, Schleiermacher has the data necessary to test Stefan's law. In this way he proves that the heat emitted from platinum, covered or not with copper oxide, increases with temperature in greater rate than Stefan's law predicts. Schleiermacher then interprets the discrepancies observed.

At the close of the present paragraph a few references to the use of the radiation pyrometer for evaluating solar temperature and others of great intensity is in place. Passing over the earlier measurements we find a paper of Soret,[2] and at about the same time one by Violle.[3] The latter's memoir is particularly complete, containing the history of the subject and a discussion of methods and apparatus. Making his observations on Mount Blanc, Violle finds 2,500° for the surface temperature of the sun. After this, observations on the temperature of flames, of the electric arc, and of the sun, were published by Rossetti.[4] Using a thermo-couple, he investigates a law of radiation as far as the boiling point of mercury, which law he carefully formulates. With due allowance for atmospheric absorption, Rossetti finds 9,965° as the sun's surface temperature. The process is, of course, one of extrapolation. The same method applied to the temperature of the electric arc gives 2,500° and 3,900° as the temperatures of the negative and positive poles respectively. A further important contribution to solar surface temperatures is due to Crova.[5]

Other optic methods of pyrometry[6] endeavor to establish the relations between temperature and the character of the spectrum. Dewar and Gladstone[7] attempted and finally abandoned a project of this kind. On the other hand, however, Stas[8] refers with some enthusiam to the

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[1] Schleiermacher: Wied. Ann., vol. 26, 1885, p. 287.

[2] Soret: Ann. de l'école norm. supér., 2d series, vol. 3, 1874, p. 435.

[3] Violle: Ann. ch. et phys., Paris, vol. 10, 1877, p. 289.

[4] Rossetti: Ann. ch. et phys., vol. 17, p. 177, 1879; C. R., vol. 89, 1879, pp. 384, 781; Philos. Mag., London, 5th series, vol. 8, 1879, p. 324.

[5] Crova: C. R., vol. 95, 1882, p. 1271.

[6] Prof. Cleveland Abbe has called my attention to a paper in the Comptes Rendus, in which the continuous change of rotation of the plane of polarization of quartz, with temperature, is made the basis of thermal measurement. Unfortunately I can not now supply the reference.

[7] Dewar and Gladstone: Chemical News, vol. 28, 1873, p. 174.

[8] Stas: Bull. Acad. Roy. Belgique, 3d series, vol. 7, 1884, p. 290.

research of Fievez,[1] in which the attempt to associate the wave-length character of the spectrum with the temperature of the source has again been made. Recently a number of German physicists have undertaken a re-interpretation of Draper's law. I have only space to allude to the papers of H. F. Weber,[2] Stenger,[3] and Kövesligethy,[4] by whom the questions relating to emission and absorption of light are being vigorously discussed. In America a series of well-known researches have been published by Langley.[5] Having perfected the bolometer, and thus developed a new method for the measurement of radiant heat and light, Langley, in a series of researches which are still in progress, has determined the distribution of energy in prismatic solar spectra and in the spectrum of the grating. Proceeding thence to artificially incandescent bodies, Langley is actively engaged in mapping out the character of their spectra for all temperature 0° to 2,000° of the source.

Less adapted for accurate measurement are certain pyrognomic substances[6] which discolor with temperature, such as the iodides of copper and mercury, for instance. To this class belong the oxide coats[7] which form on iron and copper. The tints, however, depend not only on the temperature but very materially on the time of exposure.[8]

Viscosity.—Very little use has been made of the viscous qualities of a substance for temperature measurement. Sir William Thomson,[9] indeed, proposed a thermoscope based on the change of viscosity of liquids, more especially of water with temperature; but it is intended for low temperatures, and does not seem ever to have been used.

In my own work I have found that kaolins and fire clays could be classified by noting the amount of sag at a given temperature and for a given time, which rods of the same form and dimensions experienced when spanning the distance between supports at a given length apart. The criterion here is flexural viscosity. Such a process would lend itself for temperature measurement conducted in a way similar to the fusion experiments in the case of alloys. It seems curious, however, that no attempt has yet been made to base pyrometric measurements on the viscosity of gases. Following Maxwell's[10] well-known investigation, the viscosity of gases is independent of the pressure and dependent only on the absolute temperature. From a theoretic point of view, therefore, such pyrometers have almost as much in their favor as

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[1] Fievez: Bull. Acad. Roy. Belgique, 3d series, vol. 7, 1884, p. 348.

[2] H. F. Weber: Wied. Ann., vol. 32, 1887, p. 256.

[3] Stenger: Ibid., 1887, p. 271.

[4] Kövesligethy: Wied. Ann., vol. 32, 1887, p. 699.

[5] Langley: Am. Journ. Sci., 3d series, vol. 25, 1883, p. 169.

[6] Hess: Dingl. Jour., vol. 218, 1875, p. 183.

[7] Fischer: Dingler's Jour., vol. 225, 1877, p. 278.

[8] Barus & Strouhal: Bull. U. S. Geol. Survey, No. 18.

[9] Thomson: Proc. Royal Soc., Edinburgh, vol. 10, 1880, p. 537.

[10] Maxwell: Philos. Mag., London, 4th series, vol. 19, 1860, p. 19; ibid., vol. 32, 1866, p. 390; ibid., vol. 35, 1868, pp. 129, 185; Philos. Trans., vol. 1, 1866, p. 249.

the air thermometer itself. The form of apparatus most easily used experimentally, viz, the platinum transpiration tube, is based on principles not quite as direct as Maxwell's law. Nevertheless Meyer[1] has succeeded in interpreting Graham's[2] data, has discussed his experimental methods, and has more recently shown that both Graham's and Coulomb's vibration methods lead to the same results. Work of this kind has also occupied Stefan.[3] In Meyer's deduction the volume of gas transpiring per unit of time under given conditions, besides depending on the pressures, the internal friction, the length of tube, involves an expression containing the fourth power of the radius of the capillary tube and the ratio of internal to external gaseous friction coefficiented by the third power of radius. Hence in such a pyrometer the coefficient of heat expansion of platinum must be somewhat carefully predetermined. According to Nichols (l. c.) this is by no means seriously difficult. Supposing a capillary platinum spiral to terminate in two larger platinum tubes (of which one may wholly envelop the other), we have given at once the effective part of the mechanism of a thermometer based on the viscosity of gases. Such a thermometer may be used as far as the melting point of platinum. For temperatures beyond this, porous fire-clay plugs in an impervious tube suggest themselves.

Acoustics.—The next year after Pouillet's fundamental research on pyrometry, his brilliant and ingenious countryman, Cagniard-Latour,[4] acting in concert with Demonferrand, proposed an acoustic air thermometer. Inasmuch as the velocity of sound in dry air is proportional to the square root of the absolute temperature, Latour and Demonferrand easily wrought out a formula in which temperature is expressed in terms of the vibrations of the fundamental note of their apparatus at the high temperatures and at normal temperatures. They estimate that the error of a comma would not exceed 30° at 1,000°. This apparatus was afterwards reinvented by Mayer,[5] who discusses its principle exhaustively. Mayer calculates tables for temperature, velocity of sound and wave length, between $-300°$ and $+2,000°$, and suggests many devices of measurement. After Mayer the same principle was emphasized by Chautard,[6] who simplified the apparatus necessary, but he expresses some doubt as to its efficiency.

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[1] O. E. Meyer: Pogg. Ann., vol. 127, 1866, pp. 253, 353; ibid., vol. 125, 1865, pp. 177, 401; ibid., vol. 143, 1871, p. 14; Wied. Ann., vol. 32, 1887, p. 642; cf. König, ibid., p. 193.

[2] Graham's original researches. See Philos. Trans., London, 1846, p. 573; 1849, pt. 2, p. 349. The suggestion of using platinum capillary tubes at high temperatures is my own.

[3] Stefan: Wien. Ber., vol. 46, 1862, p. 495.

[4] Cagniard-Latour et Demonferrand: C. R., vol. 4, 1837, p. 28.

[5] Mayer: Pogg. Ann., vol. 148, 1873, p. 287.

[6] Chautard: C. R., vol. 78, 1874, p. 128; Pogg. Ann., vol. 153, 1874, p. 158.

Thermo-electrics.—The use of the thermo-couple for high temperature pyrometry was suggested and carried to a high state of perfection in the great research of Pouillet.[1] He used iron and platinum for his couple. Subsequent observers suggested a wide range of substances for the purpose, and improved the methods of electrical measurement and thermal comparison, the best of them, however, following very closely in the footsteps of Pouillet's research. Solly[2] proposed an iron-copper couple, without, however, attempting to calibrate it. Regnault[3] tested an iron-platinum element but failed to obtain satisfactory results. This unfavorable dictum of the great experimentalist is much to be regretted, for it was probably the main reason which threw the subject of thermo-electric pyrometry into undeserved disrepute. Fortunately Becquerel[4] resuscitated the method, and in his hands it led to the new results cited above. Becquerel's elements were of platinum and palladium, of two different kinds of platinum, and of platinum and iron, among which he preferred the former. After Becquerel, Schinz[5] began thermo-electric pyrometry with great vigor and success, and it is indeed curious that Schinz's work is so little known. His iron air thermometer, adapted specially for calibration work, has been already described. Its chief merit is this, that an iron tube closed within, projects from the base of the cylindrical bulb into the interior. This tube, being co-axial with the stem of the bulb and the bulb itself, serves for the introduction of the thermo-couple, the junction of which may thus be exposed at the center of figure of the bulb. The re-entrant form of bulb, to which I myself was led in my experiments quite independently of the almost unknown paper of Schinz, I regard essential to accurate and expeditious calibration work. Deville and Troost[6] condemned bulbs of any other than spherical form, though, it seems to me, quite unjustly and without sufficient evidence against them. In thermo-electric comparisons the chief end in view is to secure identical conditions of exposure for the junction of the couple and the bulb of the thermometer; for the errors which result if this identity does not obtain, are apt to be much more serious than such as are due to small irregularities of contraction of the bulb. It does not seem proven, moreover, that a bulb will not contract regularly if its form is not spherical. Schinz's bulb is a large iron box, with which fine measurements can not possibly be made. The apparatus, moreover, is not at all adapted to the comparison of results obtained with different bulbs, a step which I regard as essential. My bulbs are of porcelain; they may be easily handled and exchanged one for another, and the whole method of exposure is such as to secure as much

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[1] Pouillet: C. R., vol. 3, 1836, p. 782; Dingler's Jour., vol. 63, 1837, p. 221.

[2] Solly: Philos. Mag., London, 3d series, vol. 19, 1841, p. 391.

[3] Regnault: Relation des Expériences, vol. 1, Paris, 1847, p. 246 (1845).

[4] Becquerel: Ann. ch. et phys., 3d series, vol. 68, 1863, p. 49.

[5] Schinz: Dingler's Jour., vol. 175, 1865, p. 87; Ibid., vol. 179, 1866, p. 436.

[6] Deville et Troost: C. R., vol. 57, 1863, p. 897.

facility of manipulation as is compatible with the character of the experiment. My object has been to place the calibration problem within the reach of the laboratory not specially equipped for high temperature work, and though I have worked independently, I am glad to defer the priority of principle to Schinz. In addition to his air thermometer Schinz invented a torsion galvanometer on the principle of Coulomb's torsion balance, for the measurement of thermo currents. This instrument also does credit to his experimental sagacity. His couple is iron-platinum, having failed to obtain reliable data with Becquerel's platinum-palladium couple. Schinz does not give any absolute data, and it is easily seen that the absolute value of results with his bulb could not lay claim to accuracy. He fails, for instance, to discern the iron anomalies of which Tait[1] subsequently made considerable study. Tait's memoir is well known. Following the suggestion of Thomson,[2] Tait makes an elaborate survey of the diagram by which the thermo-electrics of metals generally are to be expressed. For the measurement of temperature Tait uses a thermo-couple of platinum and platinum-iridium alloy, and, so far as I have been able to find, his researches are the first in which the pyrometric use of the platinum iridium alloy is recorded. I may add here that special attention to the platinum-iridium alloys seems first to have been given by Deville and Debray,[3] to whom we owe so much of the metallurgy of the platinum group.

A special study of the thermo-electrics of platinum-iridium and other alloys is due to Knott and MacGregor.[4] Diagrams are investigated for these alloys, applying between 45° and 400°, and for compositions as high as 20 per cent. of iridium. They also study silver-palladium, iron-gold, and platinum-silver alloys with the same ends in view. In a late research Knott, MacGregor, and Smith[5] determine the thermo-electrics of cobalt. Having studied the platinum-iridium alloy calorimetrically, Le Chatelier[6] suggests the occurrence of an allotropic modification of the alloy above red heat, the behavior being the same as that shown by iron at about 700°, and between the melting points of silver and gold. Furthermore, with the object of checking the formulæ of Avenarius[7] and Tait,[8] Le Chatelier[9] avails himself of the fusing points of Violle. It appears that these formulæ apply up to a certain temperature, above which ("brusquement") a second formula with new constants is applicable. Platinum, platinum alloys of iridium, copper and rho-

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[1] Tait: Trans. Royal Soc. Edinburgh, vol. 27, 1872–'73, p. 125.

[2] Thomson: Philos. Trans., London, vol. 146, 1856, p. 649.

[3] Deville et Debray: C. R., vol. 81, 1875, p. 839; Cf. Ann. ch. et phys., 3d series, vol. 56, 1859, pp. 431 (iridium), 415 (rhodium).

[4] Knott and MacGregor: Trans. Royal Soc. Edinburgh, vol. 28, 1876–'77, p. 321.

[5] K., M., and S.: Proc. Royal Soc. Edinburgh, vol. 9, 1876–'77, p. 421.

[6] Le Chatelier: Bull. Soc. chimique, Paris, vol. 45, 1886, p. 482.

[7] Avenarius: Pogg. Ann., vol. 119, 1863, p. 406; Ibid., vol. 149, 1873, p. 372.

[8] Tait: Trans. Royal Soc. Edinburgh, vol. 27, 1872–'73, p. 125.

[9] Le Chatelier: C. R., vol. 102, 1886, p. 819.

dium, and palladium are tested, and he finds that high temperature measurements thermo-electrically made can be relied upon to 20°. "Il résulte de mes recherches," adds he, "que la loi d'Avenarius et Tait continue à se vérifier au-dessus de 400° avec une approximation égale à celle qu'elle comporte au-dessous, jusq'à une certaine température limite, variable avec la nature des couples considérés." The superiority of the platinum-rhodium couple[1] of Le Chatelier's (which is his special contribution to thermo-electric pyrometry) over the iron platinum or platin-palladium couples is due to greater homogeneity of the former, and the fusing point calibration may be considered accurate within 5° C. In a very full paper recently published, Le Chatelier[2] shows that the condemnation which was inflicted on Pouillet and Becquerel's methods was thoroughly unjust. Believing the fusing and boiling point method of calibration to be superior to direct comparison with the air thermometer, he selects the series, H_2O (100°), Pb (323°), Hg (358°), Zn (415°), S (448°), Se (665°) Ag (945°), Au (1045°), Cu (1054°), Pd (1500°), Pt (1775°), most of which values are due to Violle (l. c.). Having, moreover, given attention to the errors due to homogeneity Le Chatelier concludes with Becquerel,[3] and many others[4] before him, that to make the Avenarius-Tait formula sufficiently applicable it is necessary either to add a cubical term or else to use two laws, one for low and the other for high temperatures. In a final memoir Le Chatelier[5] invents an ingenious method for fusing point measurement, and compares his results with those of Carnelley (l. c.). The table given contains data for alkaline and metallic chlorides, cast-irons, nickle, etc., and the paper ends with an investigation of the temperature of chemical phenomena in which heat is absorbed or disengaged, or in which the substances undergo transformation.

Finally, I desire to add that the thermo-electric effect of changes of physical state and of molecular changes in general, has not been left unnoticed. Obermayer's[6] experiments largely refer to alloys which melt at comparatively low temperatures. Tidblom[7] investigates an amplified form of the thermo-electric equation, in which changes of the kind in question may be allowed for.

Electrical conductivity.—The measurement of temperature in terms of electrical conductivity was not attempted at so early a date as the thermo-electric methods. Müller[8] attempted to co-ordinate temperature and resistance both for iron and for platinum, without, however, more than estimating the thermal datum. A resistance thermometer,

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[1] Le Chatelier: Bull. Soc. chimique, Paris, n. s., vol. 47, 1887, p. 2.

[2] Le Chatelier: Jour. de physique, vol. 6, 1887, p. 23.

[3] Becquerel: Ann. ch. et phys., Paris, 3d series, vol. 68, 1863, p. 49.

[4] Cf. Mousson: Physik, Zürich, 2d ed., vol. 3, 1874, p. 384.

[5] Le Chatelier: Bull. Soc. chimique, Paris, n. s., vol. 47, 1887, p. 300.

[6] Obermayer: Wien. Ber., vol. 66, pt. 2, 1872, p. 63.

[7] Tidblom: Beibl., vol. 1, 1877, p. 151.

[8] Müller: Pogg. Ann., vol. 103, 1858, p. 176

suggested by Quincke, was carried out practically by Reissig.[1] This is simply a wheatstone-bridge adjustment, not different in any essential respect from C. W. Siemens's[2] pyrometer, except in so far as the latter endeavored to calibrate his electrical apparatus by the calorimetric method. Siemens's pyrometer is too well known to need special description. In the final form, currents are measured electrolytically, and to give the method greater sensitiveness two identical voltameters to correspond to the hot and the cold wires are used simultaneously. This makes the apparatus to some extent independent of the local and time errors of the galvanometer. Siemens's resistance-temperature measurements are made with platinum, copper, and iron, and the data obtained are formulated.

Siemens's pyrometers were tested by Weinhold (l. c.) and pronounced sufficiently in keeping with the air thermometer to be of reliable service to the metallurgist. After this Forster,[3] Williamsen,[4] and Fischer[5] find that the effect of long-continued exposure of a Siemens pyrometer is an increment of the resistance of the exposed wire. Recalibration from time to time is therefore essential. An important series of measurements of the relation between resistance and temperature was made for quite a number of metals by Bénoit.[6] His temperatures run as high as 860° (boiling point), and all the relations are formulated. Iridio-platinum wire was tested with regard to its resistance at 15° and at white heat by Bucknill.[7] Formulæ applying for silver-platinum, iron-gold, and platinum-iridium alloys were computed with great care and from many experiments by MacGregor and Knott;[8] but their ranges of temperature did not much exceed 150°. A critical comparison of the data of the resistance temperature formulæ of Siemens (l. c.), Bénoit (l. c.), which apply for platinum, was made by Nichols,[9] and the discrepancies between these results fully pointed out. Nichols, moreover, expressed resistance in terms of his dilatation thermometer. Perhaps one of the most careful measurements of resistance as varying with temperature, and indeed the only ones which to my knowledge were made at high temperatures and by direct comparison with the porcelain air thermometer, are due to Schleiermacher.[10] This observer wrapped his wires directly around the thermometer bulb or exposed them in similar unexceptionable ways. Recognizing the variable character of ordi-

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[1] Reissig: Dingler's Jour., vol. 171, 1864, p. 351.

[2] Siemens: Proc. Royal Soc. London, vol. 19, 1871, p. 443. Dingler's Jour., vol. 198, 1870, p. 394; ibid., vol. 209, 1873, p. 419; ibid., vol. 217, 1875, p. 291.

[3] Forster: Chemical News, vol. 30, 1874, p. 138.

[4] Williamsen: Dingler's Jour., vol. 210, 1873, p. 176.

[5] Fischer: Dingler's Jour., vol. 225, 1877, p. 463.

[6] Bénoit: C. R., vol. 76, 1873, p. 342.

[7] Bucknill: Jour. Soc. Tel., Eng., vol. 7, 1878, p. 327.

[8] MacGregor and Knott: Trans. Royal Soc. Edinburgh, vol. 29, 1880, p. 599.

[9] Nichols: Am. Jour. Sci., 3d series, vol. 22, 1881, p. 363.

[10] Schleiermacher: Wied. Ann., vol. 26, 1885, p. 287.

nary platinum, he does not attempt to formulate his data. A final and more ambitious attempt to express the resistance of temperature relation is due to Callendar.[1] Wishing to establish a strictly comparable standard of high temperature, he avails himself of pure platinum. This he compares directly with an air thermometer as far as 600°. A feature of the experiments is the inclosure of the wires *within* the bulbs of the air thermometer. Great care is taken to guard against surface condensation of gas. Data are tabulated. The work enjoys the supervision of J. J. Thomson.

From a theoretical point of view the electrical conductivity of gases presents many phases available for temperature measurement. Experiments on the conductivity of hot gases are due to Buchanan.[2]

I am aware that Mr. C. A. Perkins, of Johns Hopkins University, has for some time been occupied with similar experiments.

Magnetism.—A magnetic thermoscope was proposed by Thomson,[3] but it is specially intended for low temperature. High temperature thermoscopes of this kind must obviously fail from the irregularity of the magnetic behavior of metals at high temperatures.

Interpolation methods.—Methods of this kind are of the utmost service and have been much in use. In the case of a furnace, whose temperature is increasing or decreasing regularly, a given unknown temperature may be fixed between two known temperatures by time-interpolation. The two or three known temperatures between which the unknown data lie may be convenient fusing points, sufficiently near together to make linear or quadratic interpolation practicable. Carnelley[4] and others have made much effective use of methods of this kind.

ADVANTAGES OF THERMO-ELECTRIC PYROMETRY.

Having thus indicated the chief methods of pyrometry so far employed, it next behooves me to state clearly in what respect the thermo-electric method deserves preference before all others. To do this I must reiterate the point of view already emphasized in the preface and from which the greater part of the present volume has been written. It is my belief that before important steps in most subjects directly bearing on dynamical geology can be made, our methods of high temperature measurement and of high pressure measurement must first be facilitated. Moreover, the solutions to be given to the thermal and to the mechanical problems must be such that the high temperatures may be measured under conditions of high pressure, and conversely.

When temperature measurements are to be made under these almost

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[1] Callendar: Proc. Royal Soc. London, vol. 41, 1886, p. 231.

[2] Buchanan: Philos. Mag., London, vol. 24, 1887, p. 287. The subject is now being vigorously discussed; but there is no space for further references here. (Schuster, Blondlot, Elster u. Geitl, and others.)

[3] Thomson: Proc. Royal Soc. Edinburgh, vol. 10, 1880, p. 538.

[4] Carnelley: Jour. Chem. Soc. London, vol. 1, 1877, p. 365.

insuperable difficulties, the kinds of pyrometers available dwindle down to a very small number. Indeed, the thermo-couple is almost the only instrument of research left. It is therefore most encouraging to find that, for purposes of high temperature measurement in general, the thermo-couple can be made to yield results which, apart from practical conveniences and easy manipulation, are warrantably as accurate as any known to us. I will summarize the advantages here in question as clearly as I can, so that they may be referred to in the bulk of the work:

1. Barring a few corrections, the thermo-couple of known properties is available for temperature measurement under all pressures. The corrections implied are those which become necessary in consequence of the changes of thermo-electric property with pressure; but these changes are slight and quite negligible in comparison with the thermal sensitiveness of the couples.

2. The temperature at the hot junction is dependent on the temperature at the cold junction and the constants of the couple only. It is independent of the distribution of temperature in the parts of the couple between the junctions. This is a great practical advantage, the importance of which is realized when temperature is to be measured under pressure.

3. The thermo-couple is capable of measuring temperature when the dimensions of the hot space scarcely exceed a physical point. Small zones of constant temperature and relatively small apparatus for heating are therefore sufficient for thermal comparisons of relatively great accuracy. In this respect the thermo-couple deserves preference to the resistance thermometer, particularly when material fusible with great difficulty is operated upon.

4. The upper limit of temperature measurement is practically infinite, and lies much above the melting point of platinum; for by using refractory alloys of platinum, iridium, rhodium, and inclosing wires of these metals in tubes of calcined lime, distinct and powerful thermo-electric effects are obtained even when the contents of the tubes are fused.

5. The electromotive forces of suitable thermo-couples are easily measurable with an accuracy of 1 in 1,000. Almost with the same accuracy may the indications observed at the beginning of any year be compared with those at the beginning of the next or any other subsequent time. The secular errors of a thermo-electric pyrometer, when properly cared for, need not be larger, relatively, than the secular errors of a mercury thermometer.

6. Many couples are known which, in addition to the desideratum of thermal sensitiveness, possess great tenacity and ductility, and are unalterable under ordinary conditions of heating.

7. The thermal indications are as nearly as possible instantaneous, and the discrepancy of the lag error is therefore a minimum or nil.

8. In view of the facts summarized in 2, insulation of the wires is not difficult even when the couple is to be used under pressure. This does not apply in case of the resistance thermometer.

9. When destroyed by silicification or metallic corrosion the thermo-couple may easily be purified by fusing it over again on a lime hearth and drawing to wire. With good metal the variation of constants thus produced is almost negligible.

10. Finally, the thermo-couple has this important property, that between temperatures lying not too far apart (100° to 200°) any intermediate temperature may be interpolated with great accuracy by the quadratic equation devised by Avenarius and Tait, and such interpolation, curiously enough, seems to be more trustworthy in proportion as temperature increases above the regions of incipient red heat. It is this property which specially recommends the thermo-couple for the measurement of relatively very small increments of temperature added to relatively large temperatures, possibly under conditions of high pressure, as is the case, for instance, in investigation relating to melting point and pressure of solids.

To use the thermo-element it is necessary to find the thermal equivalent of the electromotive force for all temperatures of the junctions. This is at present possible only by making detailed comparison with the air thermometer. An experimental problem of some difficulty is thus encountered at the outset. Inasmuch as the measuring part of a thermo-couple is not much more than a sensitive point, and the corresponding part of the air thermometer is a sphere of relatively enormous dimensions, it is not easy to devise an environment which at temperatures high and low shall be thermally identical for both. When temperature varies, the indications of the air thermometer necessarily lag behind those of the thermo-element. It is therefore one of the chief purposes of the present volume to devise a method such that the observed indications of air thermometer and thermo-element may be rigorously equivalent; in other words, to carry forward the methods of calibration to a degree of perfection subject only to the improvement of the air thermometer. I hope in some future publication to show the feasibility of a fire-clay air thermometer which will be available for temperature measurement much above those at which porcelain becomes too viscous for further use; but in much of the present volume the object is less to devise new methods, than to bring the old ones more within the scope of easy application than has hitherto been done. However, in Chapter V I submit a new method of pyrometry.

In calibrating thermo-couples I make use of two methods. The first of these is preliminary. The measurements made are based on known values of high boiling points. The second method, however, is a direct calibration with the air thermometer. In this way I arrive at an ultirior result; for a comparison of the two sets of data thus obtained is to some extent a criterion of the degree of accuracy with which thermal data in the regions of high temperature are known. Beyond this incidental result I do not attempt to fix the absolute value of any high temperature datum. To do this it is not only necessary to expend more time than I have now at my disposal, but it is expedient that the observer be specially equipped for the purpose. In the problems of this volume, on the other hand, where the end chiefly in view is the trial of available methods rather than the investigation of new and accurate results, such equipment is superfluous. In one case the variables of the thermal apparatus selected, including of course the limits of variation of its constants, are chiefly to be studied; in the other case additional time and pains must be spent in the absolute evaluation of the constants themselves.

CHAPTER I.

THE DEGREE OF CONSTANT HIGH TEMPERATURE ATTAINED IN METALLIC VAPOR BATHS OF LARGE DIMENSIONS.

By C. BARUS AND W. HALLOCK.

EXPLANATION.

The general character of this chapter is introductory. The experiments are therefore largely arranged with reference to a single point of view, viz, the degree of constancy attainable in metallic vapor baths at temperatures either high or low. To secure this end we profited by the experience of Messrs. Deville and Troost, who recommend the use of large masses of metal, and consequently large forms of boiling-point apparatus. The advantages gained in this way are twofold. It is obvious that if the quantity of substance used is indefinitely large, not only may the ebullition be prolonged for a considerable time—a great desideratum when many pyrometers are to be calibrated—but in the same measure, as the volume of vapor and consequently the space of constant temperature is larger, the probability of constant temperature at any one central point is proportionately increased.

There is, however, a second point of view from which the present experiments have been pursued. The questions to which this leads us do not conflict with the main purpose of the chapter. They are intimately connected with the thermal equivalents of the thermo-electric indications of small temperature variations upon which many of the following data must be based. The refractory alloys best adapted for measurements of high temperature are invariably of platinum body, in which relatively small amounts of the foreign metallic ingredient are added to platinum. This will be seen more fully below. Now it appears that alloys containing platinum and the other metal mixed in nearly equal amounts are either brittle or otherwise unsuited for wires. Often the second ingredient is of a relatively volatile or oxidizable kind. Escaping at high temperatures, this gives rise to changes of homogeneity or even of composition. Fortunately it is not difficult to find low percentage platinum alloys, which, when combined with pure platinum thermo-electrically, show electromotive forces so large that no difficulties of measurement can be apprehended. In fact the purely electrical measurement is a part of the problem which may be solved with extreme nicety.

Having these desirable properties of many platinum alloys in mind, it is a natural step in the argument to inquire into the nature of refractory alloys of platinum with gradually vanishing amounts of other metals or alloys. Given, for instance, a series of thermo-couples, one element in all of which is platinum and the other element an alloy of platinum in which the foreign ingredient diminishes from element to element in given small amounts. The limiting case of such a series is a thermo-element of pure platinum thermo-electrically combined with pure platinum. Now, a priori, it does not seem improbable that the series may possess certain properties in common, from the totality or grouping of all of which the properties of the thermo-couple platinum-platinum may be warrantably predicted, and that therefore thermo-electric measurement may actually be made by the limit couple platinum-platinum in question. The interest which attaches to any such endeavor is naturally enhanced by the fact that the said limit couple is possibly, though not necessarily, the point of convergence of any other series of alloys. In general, if any number of series of platinum alloys be made, in each of which series platinum is alloyed with small quantities of the same foreign metal, in amounts which diminish from alloy to alloy as far as zero; if, moreover, the individual members of the divers series in question be thermo-electrically combined with pure platinum, then it is not impossible, inasmuch as the thermo-electric properties of all the series converge in the thermo-electric properties of the element platinum-platinum, that a reduction of all thermo-electric data to this limit couple may be feasible. We state distinctly that the identity of the limit couple for all series is a possible case. It is not a necessary case, for the interpretation to be given to the limit couple may be different for each of the divers series which converge in it. Again, since the thermo-electrics of an alloy bear no easily discernable relation to the thermo-electrics of its ingredients, it follows that the said interpretation is far from being simple, and that the question at issue is one which must be solved experimentally.

APPARATUS.

Remarks.—The construction of apparatus for obtaining spaces of practically constant temperatures is a step introductory to all experiments in thermometry. It is important and even necessary, moreover, that the temperature be of the nature of a fixed datum; in other words, that it have always the same value under like easily reproducible circumstances, whether this value be known or unknown. To obtain such constant temperatures use has always been made of the boiling points of liquids; and boiling points conveniently disposed in the thermometric scale are at hand for selection, in the results of many observers.[1] More especially for the high temperatures we are indebted

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[1] Cf. Carnelley: Melting and Boiling-Point Tables; Landolt and Böernstein: Physikalisch-chemische Tabellen, etc.

to the classical researches of Messrs. Deville and Troost. Availing ourselves of these, we adopt vapor baths, and in the present chapter uniformly adhere to them, all the temperatures chosen for calibration or definite comparison being boiling points.

With the exception of certain forms of bath for boiling points below 100°, our apparatus consists essentially of a closed crucible provided with an axial tube for the efflux of vapor. This tube projects inward or upward as far as the center of figure of the crucible, and downward through the bottom, of which it is a part. Distillation therefore takes place per descensum, through the tube, and the surface of the surrounding boiling liquid is kept as nearly as possible at constant level as regards its position in the crucible. In the case of low boiling points this apparatus is made of metal and appropriately jacketed. For high boiling points, crucibles of graphite or of clay are preferable. In the interior of the central tube and near the center of figure of the crucible the temperature is satisfactorily constant. Here, therefore, is placed the essential part or "explorer" of the pyrometer to be calibrated. It is thus exposed in the current of vapor circulating through the tube, the walls of which are permanently kept at the boiling point by the boiling liquid surrounding them. In this way a comparatively simple form of apparatus, available at all temperatures, both high and low, retains all the essential features of the ordinary boiling point apparatus; and it is only for very low temperatures ($< 100^\circ$) that a special form is expedient.

Low boiling points.—To describe in passing this form of apparatus for low temperatures ($< 100^\circ$), we insert Fig. 1, in which the position of the thermo-element is indicated by *t a T*. The cold junction *t* is kept at constant and comparatively low temperature by water coming directly from the water mains and continually circulating around it. This cold water is further used in condensing the vapor after circulating around the hot junction *T*. A glance at the cut will make the disposition clear. Water enters at *w* and vapor at *v*, and after passing around the junctions *t* and *T*, respectively, they enter the condenser, diagrammatically shown at *cc*, the water entering an external compartment and the vapor an internal compartment. The condensed vapor is at once refed into the boiler or flask, thus enabling the observer to use this apparatus quite as long as desirable without interruption. At the cold end of the condenser the inner tube is in communication with the air. Ebullition thus takes place under atmospheric pressure. The apparatus is available for experiments with ether, methyl alcohol, alcohol and water. It fails, so far as practical convenience is concerned, for aniline, etc., because of the difficulty encountered both in conveying the vapor into it from the boiler without condensation, and because of the corrosive action of such vapors on the corks and rubber tubing of the apparatus. If made of a single piece of glass it is too liable to break at the fused joints. In the form used the tubes *v T* and *wt* were about 25^{cm} long and about 2.5^{cm} wide.

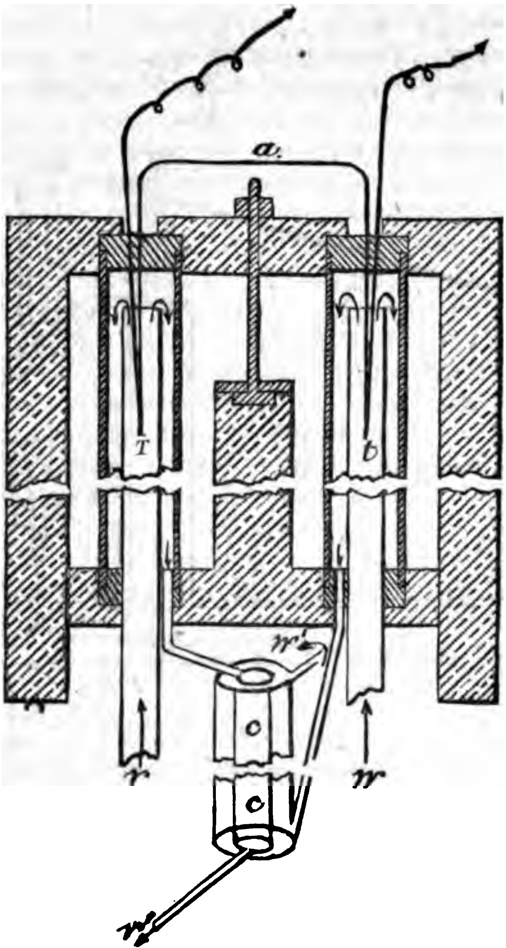

FIG. 1. Apparatus for constant temperature between 0° and 100°. Scale, ½.

Boiling points between 100° *and* 300°.—In Fig. 2 we give a form of apparatus constructed on the typical plan indicated above, and which is adapted to temperature between 100° and 300°. It consists essentially of a large sphere, *A A A*, of copper, 25^{cm} in diameter, the joints of which are brazed.

Through the bottom of this a somewhat conical central tube, *d d*, projects into the interior as shown, the tube communicating below with an iron gas-pipe, *e f g h*, leading to the condenser. The neck or head, *k*, of the spherical copper bottle is in connection with a wide glass tube, *k m*, kept in place by a gallows adjustment, the top of which, *m*, is of iron and provided with two lateral steel rods or bolts. These being fastened below to a wide flange in the neck *k*, secure the tube by screw pressure between the head *m* and the flange of *k*. It is often convenient to use gaskets of asbestos or any other kind of packing at the upper and lower end of the tube. The head *m*, moreover, is in communication with the condenser by means of the lateral tube of gas pipe, *m n o g*. Hence the vapor arising from the surface of boiling liquid, *a a*, can escape either above or below, and the respective circulations are regulated by a faucet, *f*. We found, however, that in case of corrosive or hot liquid, *f* soon begins to leak, and that it is advantageous to partially stop up the lower passage by a ball suspended in the cone *d d* from a platinum wire passing through *k m l*. In this way the use of the cock *f* may be avoided.

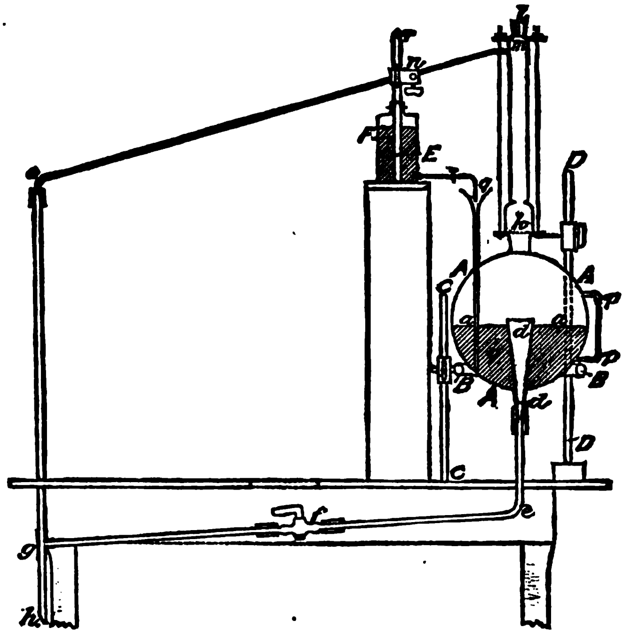

FIG. 2. Apparatus for constant temperature between 100° and 300°. Scale, $\frac{1}{15}$.

To heat the sphere *A A A* we used a large ring burner, *B B*, about 22^{cm} in diameter and provided on its inner surface with 130 jet holes, 0.15^{cm} each in diameter. This ring burner was so made that it could be used either with or without blast, according as temperatures relatively low or high were to be obtained. Its position is adjustable at pleasure by a clamp attached to the standard *C C*. Another clamp attached to the standard *D D* acts as a safeguard against lateral vibrations of the sphere *A A A*, the main weight of which is supported by the exit pipe *d e f* to the upper end of which it is screwed. A final clamp and standard, *E r*, facilitates the adjustment of the exit pipe *o n m*. The sphere is provided with a feed pipe, *q q*, and an appropriate gauge, *p p*, to register the height of the liquid. The capacity of the retort is about one gallon of liquid. If the liquid be fed in drops from a Mariotte flask, *F*, no interruption of ebullition need take place.

In the apparatus given in the figure a space of constant temperature nearly 3^{cm} wide and fully 60^{cm} long is available. If the ring burner be so adjusted that the ebullition is fairly brisk the temperature within this space is almost perfectly constant. For relatively high temperatures it is generally advisable to discard the glass tube *k m*, and to close the neck with a plate of metal suitably perforated to allow the introduction of thermo-couples. In general, however, the large tubular space is convenient both for the comparison of long-stemmed mercury thermometers and for the further comparison of electrical pyrometers with them.

We omit special data relative to the degree of constant temperature here obtained, because it is questionable whether at these relatively low temperatures the use of large forms of vapor baths is to be recommended, and because none of the data of importance below depend upon the perfection of the large retort here described. In Chapter II data for smaller forms are fully given, and from these the efficiency of the larger forms may easily be inferred.

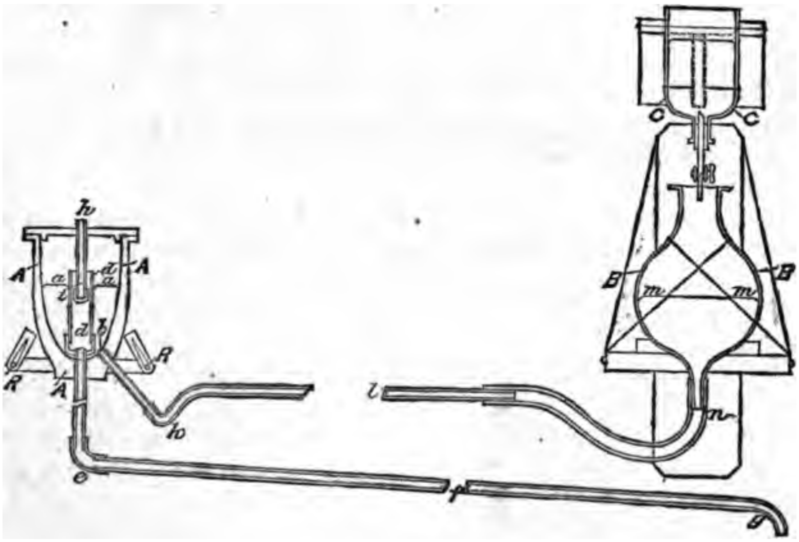

FIG. 3. Boiling-point apparatus for mercury. Scale, $\frac{1}{10}$.

Apparatus for mercury.—The boiling-point apparatus just described is useful for substances boiling at a lower temperature than mercury when constancy of boiling point can not be accurately relied upon. Such substances are mostly of organic kind, and are apt to change their properties slightly after long ebullition. It is for this reason that the mercury thermometer remains indispensable. When, however, the boiling point is fixed and known, like that of mercury or sulphur, the apparatus and the manipulations may be simplified. A form of vapor bath specially adapted to mercury calibrations is given in Fig. 3, one-tenth actual size. The boiler or retort *A A A* is of cast-iron, and is a modified form of the well-known mercury still of the shops. By drilling a hole through the bottom and tapping into it a long nipple, the central tube *d d* may be screwed down firmly in position. The nipple communicates below with a long tube of gas pipe, *e f g*, leading to the condenser. The crucible *A A A* is closed above by a flat lid, the edge of which as well as the rim of the crucible has been carefully turned, and is held in place by a stout gallows connection not shown in the figure. Through the center of the lid passes a smaller iron tube, *h t*, the lower end of which is closed and projects into the central tube *d d*, somewhat below the level *a a* of the surrounding mercury. It is into the tube *h t* that the hot junction of the thermo-element is to be introduced as far as the base of the tube. A lateral tube, *b k l n*, largely of iron, subserves the purpose of replacing the mercury lost by evaporation, and communicates with a larger reservoir, *B B*, in which the mercury is practically at the same level, *m m*, as in *A A*. Hence the level in *B B* is to some extent a gauge of the level in *A A*. A supply reservoir, *C C*, enables the operator to keep *m m* at constant height. To keep up the ebullition we made use of a kind of ring burner, consisting of three distinct blast-burners symmetrically placed around the crucible, the flames impinging upon its sides. In this way full advantage was taken of the current of air furnished by Professor Richards's pneumatic pump. The operation of boiling may therefore be prolonged indefinitely.

In the tables below we give a series of results by which the constancy of temperature attained during the successive stages of improvement of this apparatus is fully exhibited. These results will show that variations in the disposition of parts is by no means without consequence.

Boiling point of zinc.—The construction of apparatus first used was carried out by Mr. Hallock, and to him the following description is due:

In our earlier experiments an attempt was made to use the large clay retorts of the shops, but after some trials we abandoned them in favor of the special forms of retort now to be described.

Having in mind the form and operation of the ordinary apparatus for checking the boiling points of thermometers a retort was constructed with a view to surrounding the thermo-element with a double jacket of the vapor in question. It soon became evident that the simpler forms were useless, owing to the condensation of the vapors and the clogging of the outlets. We were thus led after trials of several other simpler forms, to test the arrangement shown in Fig. 4 and constructed as follows:

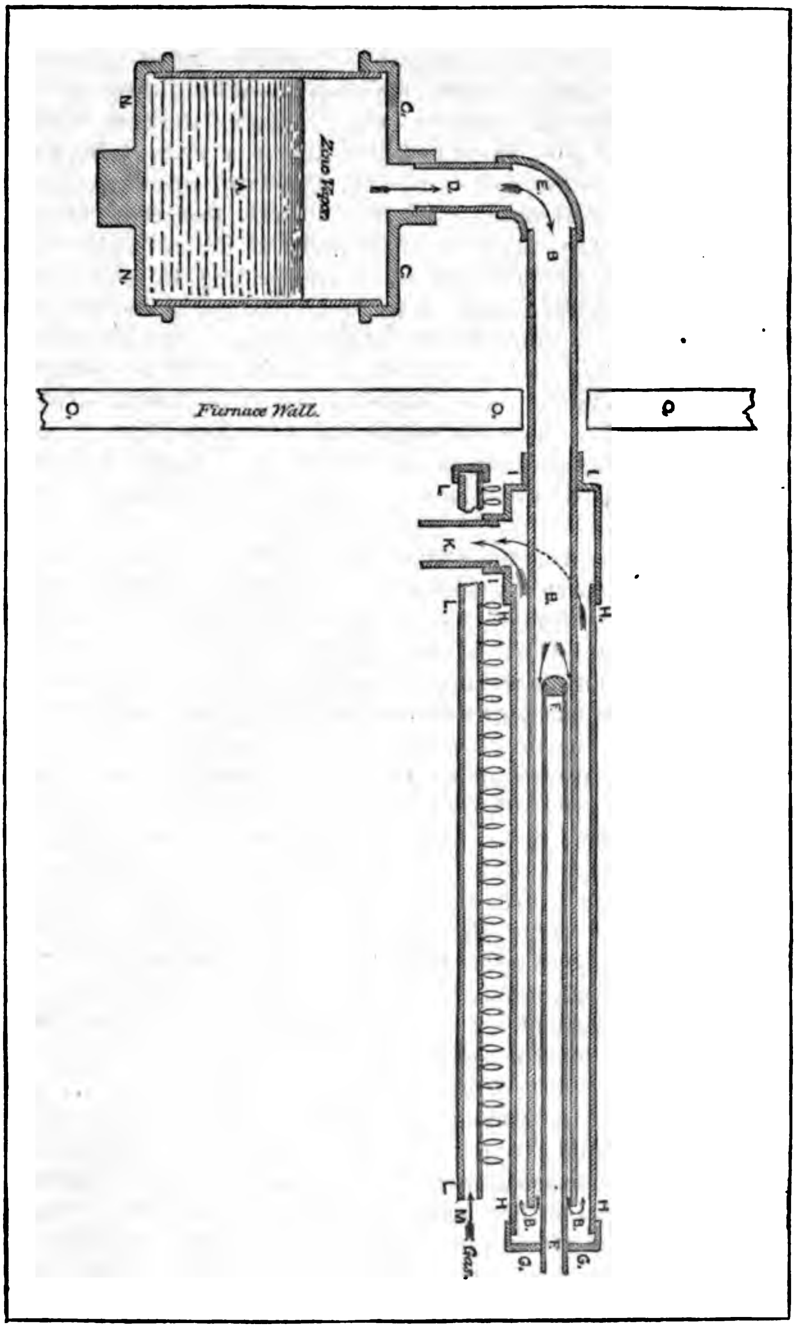

Fig. 4. Boiling point apparatus for zinc; earlier form. Scale, ½.

The cylindrical reservoir, or retort proper, shown at *A*, Fig. 4, was made by screwing cast-iron caps *N N*, *C C*, upon the ends of a piece of iron pipe 6 inches long and 6 inches in diameter. A piece of 1-inch iron pipe, *D*, fitted in the upper cap *C C*, and extended upward to an elbow, *E*, and similar pipe, *B*, which latter passed out through the side wall of the anthracite furnace at *O O*. Thence the pipe *B* extends through the T at *I I*, 18 inches, into the iron pipe *H H*, which is screwed into the other end of the T. The third opening of the T is fitted with the short outlet pipe *K*, 1 inch in diameter. A cap, *G*, closes the whole apparatus except the outlet at *K*. A small iron pipe, *F F*, passing through the cap *G*, and extending 15 inches into the interior tube *B B*, and closed at its inner end was intended to receive the thermo-element. A perforated tube burner, *L L L*, Fletcher system, placed beneath the pipe *H H*, was intended to prevent the solidification of the metal therein and consequent stoppage of the circulation of vapor. We hoped to be able with this apparatus to obtain a region of constant temperature in the inner end of the tube *F*, which would be surrounded by two distinct jackets of the vapor of zinc. We expected the action to be as follows:

The vapor rising from the boiling zinc in the retort *A*, to pass through *D* and *B B*, out past the end of *F*, out of the end of *B* into *H H*, thence backward through *H*, and out at *K*, either still in the state of a vapor or condensed to a liquid in *H*.

Two difficulties made the apparatus impracticable. Whereas melted zinc or zinc vapor has little or no solvent effect upon iron, still zinc just at the boiling surface or at the point of condensation of the vapor does dissolve iron in considerable quantities. This action of the boiling zinc soon eats through the iron walls of the retort and makes the whole apparatus very short lived. Moreover, the spontaneous combustion of zinc vapor on coming to the air inevitably results in stopping up the outlet, causing the destruction of the apparatus. These objections, together with other minor ones, led to the abandoning of this form and ultimately of all forms constructed on a similar principle.

The principle next applied was that of downward distillation through the bottom of the crucible, a system that had already proved very good for mercury and some other substances, and which has been touched upon in an earlier part of this chapter.

The particular form ultimately constructed is shown in vertical cross-section in Fig. 6 and in vertical longitudinal section in Fig. 5. In this case the furnace formed an essential part, and was constructed simultaneously and as part of the whole. It covered 5 x 3½ feet on the floor and stood 5 feet high. It was built of brick, lined with fire-brick, on the double-reverberatory principle, entirely symmetrical. Each side was provided with a fire-box, *A* (Fig. 5), a grate, *O*, ash-box, *B*, ash-door, *C*, blast inlet, *Q*, and fire-box door at *D*. The zinc was contained in the graphite crucible *F F*, which was 14 inches high, 11 inches in largest diameter, and ¾ inch thick. The graphite cover *M M* was luted on with a paste of powdered graphite and water. Through the cover *M M* the iron tube *L* passed, extending downward into the crucible and closed at its lower end. An iron pipe, *G*, 1½ inches in diameter, passed up through the bottom of the crucible about 6 inches, carrying the fire-clay spherical shell *K K*, and protected by a coating of fire-clay, *I I*.

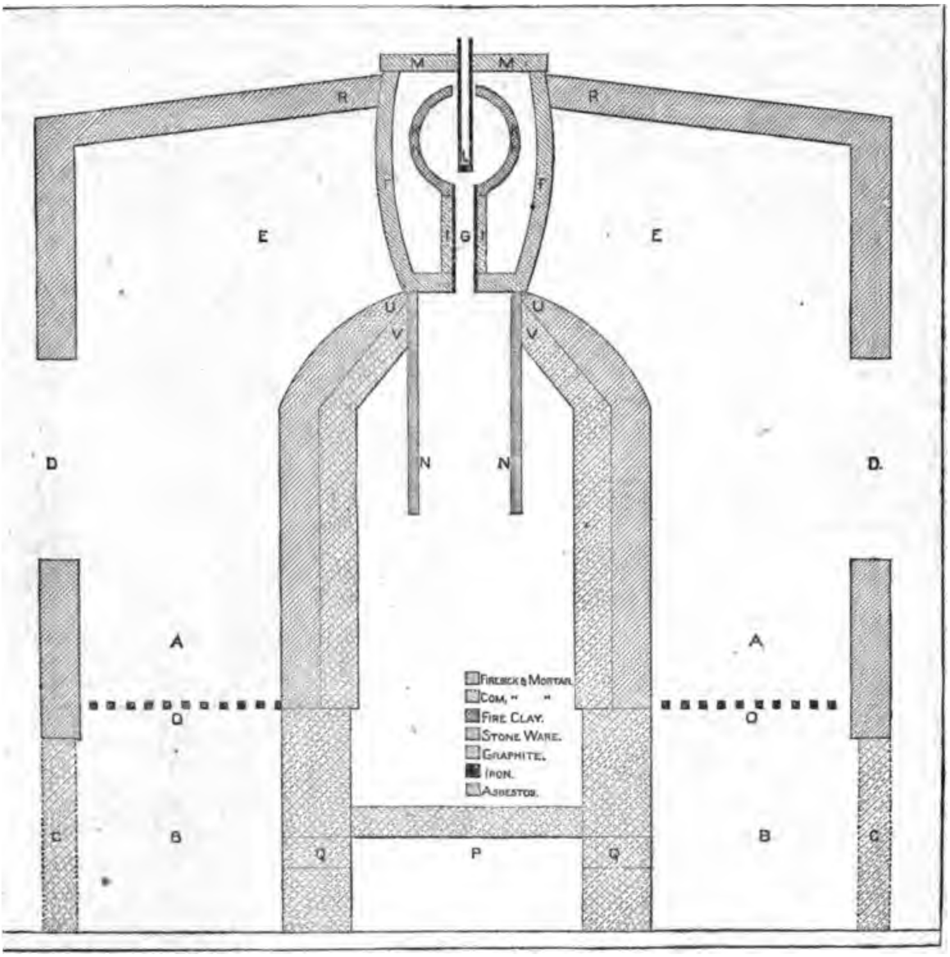

FIG. 5. Boiling-point furnace for zinc; later form; longitudinal section. Scale, $\frac{1}{12}$.

Underneath the crucible a piece of stone-ware pipe, 6 inches in diameter, *N N*, was built into the furnace concentric with the crucible and extending 15 inches below it. In practice this pipe *N N* dips just below the surface of the water in a tank placed between the two fire-boxes *A A* and not shown in the drawing.

Fig. 6 shows a vertical section through the axis of the crucible at right angles to that shown in Fig. 5. The lettering in each case is the same. *U* and *V* are the supporting arch between the two fires, and *T T* are flues to carry off the products of combustion. *R R* is the top of the furnace, *S S* are supporting columns, *W* is the entrance of the blast, and *P* the wind-box opening into the fires by *Q Q*, shown on Fig. 5.

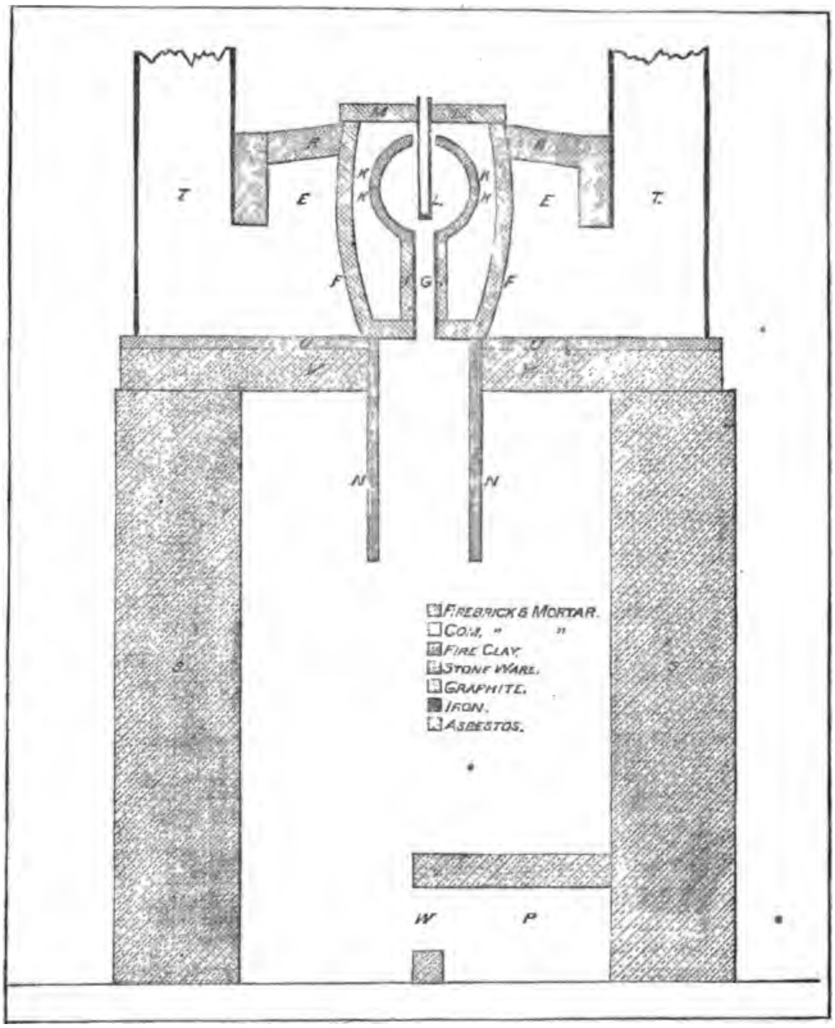

FIG. 6. Boiling-point furnace for zinc; later form; cross section. Scale, $\frac{1}{12}$.

The fuel used in this furnace was anthracite coal with a blast furnished by a 20-inch fan-blower, the ash-box door being of course closed during operation. The flames from the fire rising through the space *E E* impinged upon the crucible and passed thence off by the flues *T T*. In practice it was found that by applying fresh fuel in small quantities alternately to the two furnaces at regular intervals (ten minutes) a comparatively constant condition could be maintained until the accumulation of ashes interfered with the draft. The furnace performed its part of the work satisfactorily, but from the large dimensions at least one day was necessary to repair damages and prepare for a new "heat," and sometimes several days were necessary to get the crucible cleaned and ready again.

The crucible was filled with pieces of zinc and the powder and grains from previous distillings, mixed with powdered charcoal as a reducing agent. The cover was luted on as stated, and the tank placed under the stone pipe *N N*. In operation the vapor from the boiling metal rose around the sphere *K* and passed through holes into it, and down through *G* into *N N*, where it condensed and fell into the water, thus keeping the pipe *L* and the thermo-element contained therein at a comparatively constant temperature. The degree of constancy actually attained will be fully discussed later. Even in this apparatus the burning of the vapor proved a source of endless and unavoidable annoyance. There seems little doubt that the vapor of zinc is even able to decompose water vapor and liberate the hydrogen, itself producing a horn-like oxide, which is quite as apt to clog the outlets as the solid metal. Owing to this, many and frequent were the cases where the "heat" proved incomplete, or a total failure, owing to stoppages and explosions or leaks. This will account for the incomplete series of determinations which may occur in subsequent tables. Before we were able thoroughly to profit by our experience the transfer of the laboratory to Washington interruoted the work and gave it a different direction.

EXPERIMENTAL RESULTS.

Methods of measurement.—Whether two given temperatures are equal or not may be shown with great accuracy and certainty by thermo-electric comparison. Thermo-couples of platinum with palladium, low percentage alloys of platinum-iridium, platinum-nickel, platinum-rhodium, platinum-cobalt, and many others, are available for the purpose. Furthermore, since comparatively small increments of temperature are here to be observed, the degree of constant temperature obtained in any given space both as regards its variation at any given point with time, as well as the distribution of temperature existing in the said space at a given time, can be fairly estimated by thermo-elements of known power.

Many observations go to show that for practical purposes we may represent the partial electro-motive force at each junction of a thermo-element by an equation of the form

$$e_T = aT + bT^2 + cT^3 + \ldots \ldots \ldots \ldots \quad (1)$$

where e_T is the (partial) electromotive force at the junction whose temperature is T, and $a, b, c, \ldots$ are thermo-electric constants rapidly decreasing in magnitude.

Hence in a couple in which the junctions are at temperatures T and t, we find by difference

$$e=e_T-e_t=a\,(T-t)+b\,(T^2-t^2)+c\,(T^3-t^3)+\ \ldots \qquad (2)$$

an equation which in most cases applies so fully that the terms of the right-hand member, whose powers of T and t are greater than the third, may be neglected.

From equation (2) follows at once that

$$dT=\frac{\frac{de}{dT}dT}{a+2bT+3cT^2+\ \ldots} \qquad (3)$$

Inasmuch as the constants a, b, c, . . decrease so rapidly in magnitude that a mean or approximate value of T may be introduced into equation (3), it appears that in proportion as the increment of temperature becomes smaller it may be measured with the same accuracy with which the constants a, b, . . have been found. Methods of measuring e and of calibrating the thermo-element will be indicated in the next chapter.

List of thermo-couples.—It is expedient to insert for future reference a list of the thermo-couples used for measurement here. In the first part of this table the wires are given in the order in which their thermoelectric powers were originally determined. The other part contains the thermo-elements used for temperature measurement. The table also contains values for the constants a and b in equation (1). In the case of Nos. 0 to 15 the calibration interval is not larger than 0° to 200°; in the others as large as 0° to 400°, or 0° to 450°. The data are referred to a zinc sulphate Daniell standard, the electro-motive force of which is assumed to be one volt. Lord Rayleigh's recent value for this standard is 1.072 volt. Hence to reduce the data to absolute units, a and b must be increased 7.2 per cent. We have refrained from introducing this correction in the first two chapters because the relative values of the data there given are alone of interest, and because of the confusion and labor which a reconstruction of the whole series of data and of graphic representations would involve.

TABLE 1.—*List of thermo-couples.*

No.	Thermo-couple.*		$a \times 10^3$	$b \times 10^6$	Where made, etc. Calibration interval.
	+	−			
0	Ag	Cu	261	174	Laboratory; 0° to 190°.
1	Ag, 5% Pt	Cu	5730	7010	Do.
2	Ag, 10% Pt	Cu	7230	10100	Do.
3	Ag, 15% Pt	Cu	8964	11830	Do.
4	Ag, 25% Pt	Cu	9641	15220	Do.
5	Pt	Cu	4024	11450	Commercial; 0° to 190°.
6	Pt soft	Cu	3222	12740	Paris; 0° to 190°.
7	Pt hard	Cu	3760	9680	Do.
8	Pt Ir 5%	Cu	906	9150	Do.
9	Cu	Pt, Ir 20%	3364	3890	Do.
10	Pd	Cu	8590	21100	Do.
11	Ni	Cu	20090	22000	Do.
12	Ni	Pt soft	17680	4900	Do.
13	Pd	Pt hard	5517	8375	Do.
14	Pt hard	Pt, Ir 20%	7197	6325	Do.
15	Pd	Pt, Ir 20%	12347	16855	Do.
16	Cu	Cu	....	....	Commercial; 0° to 190°.
17	Pt hard	Pt, Ir 20%	7660	3900	Paris; 0° to 450°.
18	Pt hard	Pt, Ir 20%	7640	3670	Do.
19	Pt hard	Pt, Ir 5%	8075	—96	Paris; 0° to 370°.
20	Pt hard	Pt, Ir 5%	8056	−91	Do.
21	Pd	Pt hard	5253	9700	Do.
22	Pt hard	Pt, Ir 20%	7640	3810	Paris; 0° to 450°.
23	Pt hard	Pt, Ir 5%	2972	475	Paris; 0° to 370°.
24	Pt hard	Pt, Ir 2%	1883	—1501	Laboratory; 0° to 370°.
25	Pt soft	Pt, Pd 3%	287	1194	Do.
26	Pt soft	Pt, Pd 10%	975	2732	Do.
27	Pt, Ir 5%	Pt, Ir 10%	2362	1525	Paris; 0° to 370°.
28	Pt, Ir 5%	Pt, Ir 15%	3838	2685	Laboratory; 0° to 370°.
29	Pt, Ir 5%	Pt, Ir 20%	4507	3982	Paris; 0° to 370°.
30	Pt com.	Pt, Ni 5%	8428	505	Laboratory; 0° to 370°.
31	Pt com.	Pt, Ni 2%	4560	48	Do.
32	Pt com.	Pt, Ni 3%	1978	519	Do.
33	Pt com.	Pt, Ir 5%	3639	1472	Do.
34	Pt com.	Pt, Ir 7%	4704	2073	Do.
35	Pt soft	Pt, Ir 20%	7180	6270	Paris; 0° to 450°.
36	Pt soft	Pt, Ir 20%	7190	6290	Do.
37	Pt soft	Pt, Ir 20%	(7200)	(6300)	Do.
38	Pt soft	Pt, Ir 20%	(7200)	(6300)	Fused over from old elements.
39	Pt soft	Pt, Ir 20%	(7200)	(6300)	Do.
40	Pt soft	Pt, Ir 20%	(7200)	(6300)	Do.

Data for the mercury vapor baths.—Returning from this digression to the subject proper, we insert Table 2 to exhibit the degree of constant temperature arrived at in the mercury apparatus. The observations are made in time series. T is the temperature of the hot junction, placed at i in Fig. 3, and t the temperature of the cold junction of the thermo-element No. 18, at the time specified in the same horizontal row. T is computed from the thermo-electric data. In the first part of the table, results are given for the case in which the thermo-element tube *h i*, Fig. 3, is simply submerged in liquid.

TABLE 2.—*Constancy of temperature in the mercury apparatus.*

No.	*t.*	*T.*	Time.		Remarks.
			h.	*m.*	
18	5.1	357	2	30	Envelope of thermo-element (tube) submerged in the boiling liquid.
	4.2	337		35	
	6.6	356	3	20	
	7.8	358		30	
	8.7	356		50	
	9.6	357	4	5	
	10.2	359		20	Envelope above liquid.
18	7.2	359	6	20	Apparatus Fig. 3, but with longer central tube *dd*.
	7.2	360		35	
Results irregular and useless; no satisfactory constancy.					
18	15.0	342	3	40	Apparatus Fig. 3, but with inner side of lid and walls heavily lined with plaster.
	17.2	357	4	30	
Results again irregular; no satisfactory constancy.					
18	9.0	353.6	12	0	Apparatus Fig. 3, with central tube projecting inward only as far as the center of figure. Apparatus without feed-pipe.
	10.0	357.5		10	
	10.8	357.5		20	
	11.6	357.2		30	
	12.6	356.9		45	
	13.8	356.4		55	
	14.8	356.5	1	10	
	15.2	356.4		15	
18	6.8	354.3	10	50	Apparatus Fig. 3, completed form.
	7.4	356.8	11	5	
	8.1	356.6	11	30	
	9.1	356.7	11	50	
	10.1	356.7	12	20	
	11.2	356.7	12	55	

Curiously enough, when the walls were lined with an inch coating of plaster above the plane of ebullition, although distillation took place with great rapidity, the thermo-element did not show the boiling point until about one hour had elapsed. Where no feed-pipe is used the temperature gradually falls as the charge of mercury diminishes in bulk. In the final form the negligible differences of temperature, amounting (after ebullition has set in) to less than 0.2°, are probably errors of measurement. The accuracy of the thermo-electric method is not warranted within 0.1 per cent.

Data for the zinc vapor baths.—In digesting the data obtained for the variation of temperature in the zinc apparatus, it will be necessary to be more circumspect. For this reason we shall exhibit a very complete set of data. Early values, i. e., such as were derived with couples of palladium or of platinum-silver alloy are discarded, because during the course of the measurements such elements were usually corroded through, and little confidence could, therefore, be felt in the use of the constants of the uncorroded element. Assuming equation (1) above, the temperature, T, of the hot junction of the couple is

$$T=\frac{a}{2b}\left\{\sqrt{1+\varepsilon\frac{4b}{a^2}}-1\right\}$$

where a and b are the constants of the element, and where, if t be the temperature of the cold junction and e the observed electro-motive force for temperatures t and T of the junctions

$$\varepsilon=e+at+bt^2.$$

This value, ε, is therefore the electro-motive force when the cold junction is at zero, other conditions remaining the same. The passage from e to ε usually involves only a small correction which may be interpolated from tables calculated for the purpose. Nevertheless the computation of T, where many results are in hand, is exceedingly tedious; and it is therefore preferable to avoid it by the use of graphic methods, as explained in Chapter II. In computing the values of T, the constants obtained in later and more refined apparatus are of course used, all older calibrations being allowed no more than corroborative importance.

In Table 3 we give some of our earlier results, the first of which were obtained by submerging a protected thermo-couple in boiling zinc contained in a large fire-clay retort. The charge was from 5 to 10 pounds, but special data are not at hand. After this the iron apparatus described in Fig. 4 was used. Owing to difficulties of manipulation, we thereupon returned to the retort pattern, providing it with a suitable condenser; exchanging this, eventually, for a graphite crucible on the general plan of Fig. 5, but of much smaller dimensions. It is in this order that the results in the tables are given. The third column of the table contains the number of kilogrammes distilled and the total number of kilogrammes of zinc charged; e_{20} is the observed electro-motive force in microvolts, nearly when the hot junction is at T and the cold junction at 20°; e_{20} is preferred to ε, which applies for $t=0°$ because t in the average case is usually in the neighborhood of 20°, and therefore the correction to be added is small. T_s and $T_{s''}$ are thermo-electric data for the boiling point, when the calibration interval within which the constants apply is respectively 0° to 450° and 0° to 1000°. T_s is therefore the result of exterpolation. Further remarks regarding these quantities must be reserved for Chapter II.

TABLE 3.—*Constancy of temperature in earlier forms of the zinc boiling-point apparatus.*

Date.	Apparatus.	Kg. of Zn. distilled; charge.	No. of thermo-couple.	e_{20}.	T_s.	T_m.
Dec. 28, 1883	Retort	1	14	9150	847	914
Jan. 10, 1884	......do	1	14	9600	880	950
Jan. 11, 1884	Iron boiling-point apparatus	....	14	9630	883	953
Jan. 15, 1884	Retort with condenser	....	14	9390	867	934
Jan. 29, 1884	Graphite boiling-point apparatus	1	18	9216	860	924
Jan. 30, 1884	.... do	5	18	9184	856	921
Feb. 2, 1884	......do	2	18	9191	857	922
Feb. 4, 1884	......do	2	18	(9281)	865	930

It is to be borne in mind that the above data have a relative significance only. Their absolute values can not be discussed before Chapter IV. The same thermal and electric scales are uniformly used throughout Chapters I and II.

In Table 4 data showing the progressive stages of temperature of the zinc crucible are given in time series. The plan is identical with that of the preceding table. *h* denotes the number of hours elapsed from the beginning to the end of the ebullition.

TABLE 4.—*Constancy of temperature in earlier forms of the zinc boiling-point apparatus; time series.*

Date.	Time.	*h*.	No. of thermo-couple.	e_{20}.	T_s.	T_m.	Remarks.
	h. m.						
Jan. 29, 1884	4 25	0.00	18	9220	860	925	Charge insufficient.
	32	0.12	18	9180	857	921	
	37	0.20	18	9170	856	920	
	48	0.38	18	9020	846	910	
	55	0.50	18	8580	815	872	Furnace cools.
Jan. 30, 1884	2 35	0.00	18	6500	658	693	Approaching ebullition.
	45	0.17	18	7510	736	682	
	3 00	0.42	18	8920	840	900	
	20	0.75	18	7800	756	807	Blower stopped by accident.
	35	1.00	18	8150	781	836	
	40	1.08	18	8910	830	899	Approaching ebullition.
	45	1.17	18	9150	854	919	
	50	1.25	18	9180	856	920	Ebullition.
	55	1.33	18	9180	856	920	
	4 10	1.55	18	9260	864	928	
	15	1.67	18	9260	864	928	
	30	1.92	18	9300	867	933	
	40	2.08	18	9370	870	938	Charge distilled.
	50	2.25	18	9610	886	956	
	5 00	2.42	18	9770	898	970	Superheating.
	10	2.58	18	9680	890	961	
	15	2.67	18	9540	882	951	Furnace cools.
	25	2.83	18	9220	860	924	

TABLE 4.—*Constancy of temperature in earlier forms of the zinc boiling-point apparatus; time series*—Continued.

Date.	Time.	h.	No. of thermo-couple.	e_{20}.	T_s.	T_m.	Remarks.
	h. m.						
Feb. 2, 1884	3 15	0.00	18	7930	768	818	Approaching ebullition.
	19	0.07	18	8100	780	833	
	25	0.17	18	8420	802	860	
	30	0.25	18	8740	825	884	
	35	0.33	18	9110	851	915	Ebullition.
	40	0.42	18	9170	856	920	
	56	0.68	18	9190	857	921	
	4 19	1.07	18	9220	860	924	

The second part of this table (Jan. 30) is complete. The third (Feb. 2) and the first (Jan. 29) part together make a series, showing in all cases the rise and fall of temperature at the inception and at the close of the distillation. The criterion of the occurrence of the boiling point is constancy of temperature; for the furnace is sufficiently hot to superheat the crucible when the charge of zinc is low or nearly distilled over as the second part of the table shows. An early stopping or a late beginning of the experiment is the result of accidents, which for the difficulty of the experiments are not infrequent.

As distinguished from the above data the following results are all obtained with very large apparatus, a "number 60" graphite crucible of Messrs. Dixon, with a capacity sufficient to hold 60 pounds of zinc, being used for the experiments. The apparatus and furnace have already been described and it will therefore suffice to summarize the data. This is done in the following very complete tables on a plan identical with the preceding.

TABLE 5.—*Constancy of temperature in the later form of zinc boiling-point apparatus; time series.*

Date.	Time.	h.	No. of thermo-couple.	e_{20}.	T_s.	T_m.	Remarks.
	h. m.						
Apr. 15, 1884	2 15	0.00	18	7980	770	822	Charge 14 pounds.
	26	0.18	18	8540	812	868	
	38	0.38	18	9110	852	915	
	50	0.58	18	9550	882	952	
	53	0.63	18	9710	893	965	
	3 05	0.83	18	9940	910	983	
	10	0.92	18	10020	915	990	
Apr. 18, 1884	2 08	0.00	18	9500	880	947	Charge 20 pounds.
	15	0.12	18	9530	882	950	
	20	1.20	18	9640	890	957	
	30	0.37	18	9807	901	971	Furnace fired.
	40	0.53	18	9960	911	985	
	60	0.70	18	9930	909	982	

TABLE 5.—*Constancy of temperature in the later form of zinc boiling-point apparatus; time series*—Continued.

Date.	Time.	h.	No. of thermo-couple.	e_{20}.	T_e.	T_{za}.	Remarks.
	h. m.						
Apr. 18, 1884	3 00	0.87	18	10020	915	990	
	10	1.03	18	10110	920	995	Do.
	20	1.20	18	10130	922	998	
	30	1.37	18	10080	920	995	
	42	1.57	18	10320	935	1013	Retort begins to leak.
	4 00	1.87	18	10480	945	1025	
	10	2.03	18	10510	948	1026	
	20	2.20	18	10500	946	1026	
	30	2.37	18	10390	939	1019	
	42	2.57	18	9910	908	980	
	3 33	0.00	18	7571	740	787	Charge 50 pounds.
	50	0.28	18	7990	772	823	Furnace fired.
	4 00	0.45	18	8230	790	844	Do.
	10	0.62	18	8570	813	872	Do.
	20	0.78	18	8870	835	897	Approaching ebullition.
	30	0.95	18	8930	839	900	Furnace fired.
	43	1.17	18	9100	851	914	Do.
	50	1.28	18	9120	852	915	Ebullition.
Apr. 24, 1884	5 00	1.45	18	9130	852	916	Furnace fired.
	10	1.62	18	9130	853	916	Do.
	22	1.82	18	....	....	....	Do.
	33	2.00	18	9140	854	917	Do.
	50	2.28	18	....	....	....	Do.
	55	2.37	18	9130	852	916	
	6 10	2.62	18	....	....	....	Do.
	20	2.78	18	9180	856	921	Do.
	31	2.97	18	....	....	....	Do.
	45	3.20	18	9190	857	922	Superheating; F. fired.
	55	3.37	18	....	....	....	
	7 05	3.53	18	9240	861	925	25 pounds distilled.
Apr. 30, 1884	1 53	0.00	18	8530	812	870	Charge 50 pounds.
	2 15	0.37	18	8970	842	905	
	26	0.55	18	9080	850	912	Ebullition.
	45	0.87	18	9140	854	918	
	3 15	1.37	18	9120	853	915	
	35	1.70	18	9160	856	920	
	57	2.07	18	9190	858	922	
	4 15	2.37	18	9220	859	924	
	36	2.72	18	9280	864	930	
	5 00	3.12	18	9340	868	934	
	20	3.45	18	9270	863	930	
	35	3.70	18	9280	864	930	28 pounds distilled.
May 12, 1884	3 00	0.00	18	7940	768	799	Charge large.
	20	0.33	18	8520	811	868	
	30	0.50	18	8760	828	887	
	38	0.63	18	8880	837	896	
	40	0.67	18	8900	838	900	
	45	0.75	18	8950	842	902	
	50	0.83	18	8960	843	904	Approaching ebullition.
	55	0.92	18	8960	842	904	
	4 10	1.17	18	8960	842	904	
	30	1.50	18	....	842	904	
	5 00	2.00	18	8980	844	906	
	15	2.25	18	9000	845	907	
	33	2.56	18	9020	846	908	

TABLE 5.—*Constancy of temperature in the later form of zinc boiling-point apparatus; time series*—Continued.

Date.	Time.	h.	No. of thermo-couple.	e_{20}.	T_e.	T_{zn}.	Remarks.
	h. m.						
May 19, 1884	3 00	0.00	18	8370	800	855	Charge large.
	15	0.25	18	8750	827	885	
	30	0.50	18	8960	841	903	
	35	0.58	18	9050	847	911	
	40	0.67	18	9050	848	911	
	4 20	1.33	18	9270	863	929	
	30	1.50	18	9590	885	955	Central tube cracks.
	5 00	2.00	18	0330	934	1012	Superheating.
May 21, 1884	3 25	0.00	18	7690	764	814	Charge large.
	35	0.17	18	8250	790	845	
	4 00	0.58	18	8630	819	876	
	10	0.75	18	9030	847	910	
	20	0.92	18	9120	853	915	
	30	1.08	18	9240	862	926	
	35	1.17	18	9310	867	932	
	40	1.25	18	9360	870	936	
	5 00	1.58	18	9500	879	948	Central tube cracks.
	03	1.63	18	9540	881	951	Superheating.
May 26, 1884	2 25	0.00	22	8840	828	890	Charge large.
	35	0.17	22	9081	845	908	
	45	0.33	22	9110	847	910	Ebullition.
	3 05	0.67	22	9160	849	915	
	15	0.83	22	9200	852	918	
	35	1.17	22	9300	860	927	
	50	1.42	22	9330	863	930	
	4 20	1.92	22	9470	874	940	
	40	2.25	22	9450	870	940	Crucible explodes.
June 9, 1884	2 15	0.00	19	....	716	(672)	Charge large.
	30	0.25	19	....	741	(696)	
	45	0.50	19	....	782	(735)	
	3 05	0.83	19	....	855	(805)	
	15	1.00	19	....	934	(880)	
	19	1.07	19	....	981	(925)	
	20	1.08	19	....	987	(930)	
	25	1.17	19	2864	987	930	
	30	1.25	(20)	....	....	....	
	40	1.42	(20)	2830	975	920	
	55	1.67	(20)	2784	960	907	
	4 10	1.92	19	2760	954	901	
	25	2.17	19	2767	954	901	
	40	2.42	19	2738	944	891	
	55	2.67	19	2737	944	891	
	5 08	2.88	19	2732	942	890	
	25	3.17	19	2755	950	890	
	40	3.42	19	2803	966	913	
	50	3.58	19	2809	968	915	
June 11, 1884	3 45	0.00	19	2808	970	915	
	55	0.17	19	....	....	....	
	4 00	0.25	19	2806	969	915	
	07	0.37	19	....	....	....	
	12	0.45	19	2848	982	925	
	18	0.55	19	....	....	....	
	25	0.67	19	2815	970	915	

TABLE 5.—*Constancy of temperature in the later form of zinc boiling-point apparatus; time series*—Continued.

Date.	Time.	h.	No. of thermo-couple.	e_{20}.	T_z.	T_{zn}.	Remarks.
	h. m.						
June 11, 1884	35	0.83	19	....	....	....	
	45	1.00	19	2815	970	915	
	50	1.08	(23)	2806	970	915	
	58	1.22	19	2828	974	920	
	5 10	1.42	19	....	....	....	
	15	1.50	19	2824	972	916	
	25	1.67	19	....	....	....	
	30	1.75	19	2784	960	907	
June 14, 1884	3 23	0.00	19	2811	970	914	
	3 47	0.40	19	2839	976	921	
June 21, 1884	4 35	0.90	23	....	999	939	
	41	0.10	23	2907	1002	942	
	55	0.33	23	2915	1002	943	
	5 06	0.52	23	2919	1004	944	
	22	0.78	23	2935	1010	950	
June 25, 1884	3 55	0.00	23	2809	970	914	
	4 15	0.33	23	2809	970	914	
	4 40	0.75	23	2829	974	920	
	4 55	1.00	23	2829	974	920	
	5 06	1.18	23	2829	974	920	
	5 18	1.38	23	2780	960	907	

In the experiments made on the 15th and 18th of April the charges were obviously too small. Hence we fail to discern a boiling point in the first instance and obtain irregular results in the second, in both of which cases the zinc vapor is superheated. In the next series the charge of zinc is much increased and the results are regular. The value of T_{zn} is slightly low, a result which may be attributed to various extraneous causes, such as slight corrosion or zincification of the thermocouple, polarization errors in the measuring apparatus, etc. In this, as in the following series of experiments of the 30th of April, the temperature of the cold junction, in consequence of its unavoidable proximity to the furnace, rises as high as 70°. Otherwise both series are as complete as any we made. The effect of charging the furnace with fresh coal does not chill the retorts perceptibly, and the experiments were carried to an end without accident. In the series made on the 12th of May, as well as in all subsequent series, the cold junction was kept at a low temperature (ca. 15°) by submerging it in a current of running water. The values for T_{zn} found are lower than usual. The work done both on the 19th of May and on the 21st of May was interrupted by breakage of the central tube. There resulted a diminution of the charge of zinc, in consequence of leakage, and the thermo-element soon indicated the presence of superheated zinc vapor. No boiling point is discernible. The experiments on the 26th of May were again terminated at an early stage of progress by an explosion, due to stoppages in the efflux pipe for the zinc vapor. Both the elements No. 18 and No. 22

were partially destroyed by these accidents, necessitating their replacement by No. 19. The constants and thermo-electrics of the new couple being different from the old, it is clear that the subsequent values for T_{zn} are no longer immediately comparable with the preceding values for T_{zn}. To make them as nearly as possible comparable, however, the following method was pursued: The values for e_{20}, corresponding to Nos. 19, 20, 23, and obtained on the 2d of February, on the 24th of April, and on the 12th, 26th, and 30th of May, were averaged, and this mean value was assumed to correspond with the mean values of T_{zn} given by No. 18 on the same days, respectively. A glance at the tables below shows that on these days one of the series of elements, Nos. 19, 20, 23, and one of the series of elements, Nos. 17, 18, 22, were simultaneously compared. From these data the constants of the former set (Nos. 19, 20, 23) and a graphic representation were investigated; from this finally we took the values of T_{zn} given in Table 5. In this way the break in the results is reduced to the least value possible under the circumstances.

It is curious that in the subsequent work we were not able to obtain series of results as satisfactorily constant as in the earlier experiments. To speculate on the causes for discrepancy is of course futile, and the later data subserve no other purpose than that of comparing the thermo-electric behavior of the couples simultaneously calibrated.

INFERENCES RELATIVE TO LOW PERCENTAGE ALLOYS.

Reduction of data.—In view of the insufficient degree of constancy observable in the above results as a whole, it is necessary to resort to an artifice by which all thermo-electric forces may be referred to a fixed interval of temperature, $T-t$. For the lower limit of this interval we selected 20°, a temperature as near the mean value of t as practicable; for the upper limit 930°, the assumed value of the boiling point of zinc. Then the reduction to the lower limit has the value

$$e_{20}-e=(t-20)\ \{a+b\ (t+20)\};$$

and the reduction to the higher limit the value

$$e_{930}-e=(930-T)\ (a+b\ (930+T)).$$

The method of correction was therefore a quadratic interpolation by which the thermo-electric interval is rectified at each end, and thus reduced to the uniform temperature interval. The constants a and b were carefully redetermined in a final calibration, so that the sole remaining difficulty in the equation is the choice of T. Fortunately it is only the variations of T with which the above equation is concerned, and this may be obtained either by linear reduction of the thermo-electric datum T_s to 930°, or we may calculate the constants for each element throughout the interval 0° to 930°, and then use the T_{zn} so obtained. The first method is less accurate than the second without being insufficiently accurate. At the same time the first method is so much more expeditious that we applied it.

TABLE 6.—*Values of e_{30}^{930}, approximately, in microvolts.*

Date.	No. of thermo-couple.	e_{30}^{930}.	Date.	No. of thermo-couple	e_{30}^{930}.
January 29, 1884	18	9160	June 9, 1884	25	935
January 29, 1884	18	9150	June 9, 1884	19	2825
January 29, 1884	18	9170	June 9, 1884	26	2361
January 30, 1884	18	9180	June 9, 1884	19	2823
January 30, 1884	18	9180	June 9, 1884	30	7147
January 30, 1884	18	9180	June 9, 1884	19	2824
February 2, 1884	18	9180	June 9, 1884	31	3738
February 2, 1884	17	9320	June 9, 1884	19	2823
February 2, 1884	18	9160	June 9, 1884	34	5367
February 2, 1884	19	2816	June 9, 1884	19	2827
February 2, 1884	18	9160	June 9, 1884	33	4011
April 24, 1884	18	9100	June 9, 1884	19	2829
April 24, 1884	22	9220	June 9, 1884	32	1982
April 24, 1884	18	9100	June 9, 1884	19	2830
April 24, 1884	23	2827	June 9, 1884	32	1974
April 24, 1884	18	9120	June 9, 1884	19	2830
April 24, 1884	24	770	June 11, 1884	19	2829
April 24, 1884	18	9100	June 11, 1884	22	9363
April 24, 1884	25	891	June 11, 1884	19	2830
April 24, 1884	18	9090	June 11, 1884	27	2908
April 24, 1884	26	2274	June 11, 1884	19	2833
April 24, 1884	18	9070	June 11, 1884	28	5030
May 12, 1884	18	9130	June 11, 1884	19	2833
May 12, 1884	22	9280	June 11, 1884	29	6482
May 12, 1884	18	9130	June 11, 1884	19	2836
May 12, 1884	23	2830	June 11, 1884	23	2830
May 12, 1884	23	2834	June 11, 1884	19	2834
May 12, 1884	18	9130	June 11, 1884	17	9250
May 12, 1884	24	786	June 11, 1884	19	2833
May 12, 1884	18	9120	June 11, 1884	18	9330
May 12, 1884	25	898	June 11, 1884	19	2828
May 12, 1884	18	9140	June 14, 1884	19	2832
May 12, 1884	26	2333	June 14, 1884	34	5349
May 12, 1884	18	9130	June 14, 1884	19	2833
May 19, 1884	18	9290	June 14, 1884	33	6762
May 19, 1884	24	780	June 14, 1884	19	....
May 26, 1884	22	9080	June 21, 1884	23	2835
May 26, 1884	19	2810	June 21, 1884	34	5291
May 26, 1884	22	9080	June 21, 1884	23	2834
May 26, 1884	20	2800	June 21, 1884	33	3951
May 26, 1884	22	9060	June 21, 1884	23	2835
May 26, 1884	22	9050	June 21, 1884	32	2018
May 26, 1884	25	852	June 21, 1884	23	2839
May 26, 1884	22	9060	June 25, 1884	23	2830
May 26, 1884	26	2205	June 25, 1884	31	3751
May 26, 1884	22	9040	June 25, 1884	23	2830
May 26, 1884	24	817	June 25, 1884	30	7095
May 26, 1884	22	9030	June 25, 1884	23	2832
May 26, 1884	22	9122	June 25, 1884	29	6416
May 26, 1884	22	9080	June 25, 1884	23	2832
June 9, 1884	19	2830	June 25, 1884	28	5029
June 9, 1884	20	2850	June 25, 1884	23	2832
June 9, 1884	19	2830	June 25, 1884	27	2974
June 9, 1884	24	791	June 25, 1884	23	2819
[illegible]ne 9, 1884	19	2830			

From this table it is expedient to select the mean values for each element, and then to arrange the alloys in a series of the kind described on page 80. This has been done in Table 7, where, in addition to $e_{20}{}^{930}$, the constants a and b, derived from the last definite calibration, are inserted (microvolts). The interval of calibration for a and b is only 0° to 400°, as has been stated. Knowing, therefore, e, a, and b we are able to compute T_s, or the exterpolated value of the zinc boiling point, to which special reference will presently be made. The figures for e in parenthesis will be referred to in Chapter II.

TABLE 7.—*General summary of results.*

Series No.	No.	Description of element.	How, where, or by whom made.	Mean e.	a.	b.	T_s.
I	17	Pt (h); Pt-Ir, 20%; annealed.	Paris metallurgists..	(9412) 9285	7.60	+0.00390	861
	18	......do	....do................	(9345) 9166	7.60	+0.00385	857
	19	Pt (h); Pt-Ir, 5%; annealed ..	....do................	(2861) 2823	3.07	−0.00010	966
	20	......do	....do................	(2869) 2827	3.05	−0.00009	973
	22	Pt (h); Pt-Ir, 20%; annealed..	....do................	(9453) 9230	7.60	+0.00393	856
	23	Pt (h); Pt-Ir, 5%; annealed ..	....do................	2829 (2885)	(2.97)	(+0.00047)	970
	24	Pt (h); Pt-Ir, 2%; annealed ..	Pt-Ir 5% fused into Pt (s) in proper ratio, at Lab., OH_2 blast.	791	1.88	−0.00150	(*)
II	25	Pt (s); Pt Pd, 3%; annealed..	Pd alloyed to Pt (s), at Lab., OH_2 blast.	982	0.287	+0.00119	797
	26	Pt (s); Pt Pd, 10%; annealed..		2297	0.975	+0.00273	760
III	27	Pt-Ir, 5%; Pt-Ir, 10%; annealed.	Pt Ir 5% and Pt Ir 20% wires fused together in proper ratio, at Lab., OH_2 blast.	2941	2.30	+0.00152	826
	28	Pt-Ir, 5%; Pt-Ir, 15%; annealed.		5030	3.89	+0.00268	834
	29	Pt-Ir, 5%; Pt-Ir, 20%; annealed.		6449	4.51	+0.00398	835
IV	30	Pt (com.); Pt(com)-Ni, 5%; annealed.	Ni alloyed to Pt (com.), at Lab., OH_2 blast.	7121	8.43	+0.00050	825
	31	Pt (com.); Pt(com)-Ni, 2%; annealed.		3744	4.56	+0.00005	833
V	32	Pt (com.); Pt(com.)-Ir, 3%; annealed.	Ir (com.) alloyed to Pt (com.), at Lab., OH_2 blow-pipe.	1998	1.98	+0.00052	844
	33	Pt (com.); Pt(com.)-Ir, 5%; annealed.		3981	3.64	+0.00147	833
	34	Pt com.); Pt(com.)-Ir, 7%; annealed.		5336	4.70	+0.00207	842

* Imaginary.

Series of alloys.—Having reached this stage of the inquiry, we are prepared, so far as the set of data at present in hand go, to bring the considerations back to the probable properties of the zero elements, platinum-platinum, when these elements are regarded as the limiting cases into which any series of thermo-couples of platinum alloys must ultimately converge. A series of couples such as is here understood has already been defined. In each member of such a series pure platinum is thermo-electrically combined with an alloy of platinum and a second metal, and the amount of the latter metallic ingredient decreases from alloy to alloy of the series as far as zero.

Having given a number of thermo-couples, *A*, *B*, *C*, *D* . . . , let the cold junction all be kept at the same constant temperature, *t*. In like manner let the hot junctions be exposed together to a second temperature, which, however, is made to vary continuously from a comparatively low value to as high a value as may be admissible. Then will a comparison of corresponding values of electro-motive force indicate in how far the variation of the latter with temperature may be regarded as uniformly continuous. Thermo-electric anomalies, such, for instance, as are presented by iron, nickel, probably by some platinum-iridium alloys, and by all metals at sufficiently high temperatures, are thus detected and located. In practice it is convenient to compare the thermo-couples in pairs; and like exposure of the hot junction is facilitated by melting them to a common spherule with the oxyhydrogen blow-pipe. A tube may be placed in Fletcher's organic combustion-furnace or in an anthracite blast-furnace and the insulated thermo-elements heated within it, with their common junction near the center of the tube. All wires so compared are supposed, of course, to be homogeneous throughout their length.

TABLE 8.—*Equivalent thermo-electric powers.*

Pt, Pt Ir 20%. No. 14.	Pd, Pt Ir 20%. No. 15.	Pt, Pt Ir 20%. No. 14.	Pt, Pd. No. 13.	Pt, Pt Ir 20%. No. 14.	Pt, Ni. No. 12.	Pt, Pt Ir 20%. No. 14.	Pt, Pt Ir 5%. No. 19.
810	1470	810	680	810	1830	2900	1028
1350	2510	1350	1150	1350	2990	8430	2605
4290	8380	2250	1990	2706	5120	8470	2610
4370	8600	4280	4200	3130	5590	8570	2500
4770	9470	5690	5970	4640	7000	9030	2660
5700	11610	7018	7860	6990	9450	9550	2720
6140	12330	7680	8830	7750	10210	13190	3090
7910	16940						
7970	17210	T =	800°	T =	800°	T =	1200°
8370	18360						
T =	850°						

At the end of this table the approximate value of the temperature reached in each of these comparisons is given. The values of electro-motive forces in this table (No. 14 being the couple common to all) show that the variations are practically uniform, so far as the comparisons go. The table supplies an experimental test, which corresponds very closely to the mathematical examination of a function for continuity.

If any equation between electromotive force and temperature, such a one, for instance, as $e=a(T-t)+b(T^2-t^2)$, were rigidly true for all ranges of temperature, T, then our methods would enable us to calculate the constants a and b from measurements of e, T, t, made at temperatures not exceeding the boiling point of mercury, with a degree of accuracy which would introduce a perceptible error only at very much higher temperatures. If the thermo-electric equation hold, in other words, the calibration of a thermo-couple throughout an interval of temperature within which a glass-bulb air-thermometer is quite available, would enable us satisfactorily to measure temperatures lying in the regions of white heat. But such extrapolation is unwarranted because we possess no known criterion for the temperature above which the assumed equation appreciably fails.

In our original endeavor to surmount this difficulty we ventured to reason as follows: Suppose there be given a series of thermo couples of the kind specified, in all of which platinum is the electro-positive metal and the platinum alloy the negative metal. In such a series the constants a and b both vanish with the amount of foreign metal alloyed to platinum. Hence the relation between electro-motive force and temperature is ultimately linear, and, a fortiori, within the limits prescribed by the foregoing paragraph, the assumed equation will apply more accurately as the couple approaches the final couple platinum-platinum, from which the foreign metal has been wholly eliminated. If the quadratic equation (1) is more than an empirical relation, it would be practically sufficient at an earlier stage of progress; i. e., it would be practically sufficient for couples lying between platinum-platinum and a couple the electro-negative part of which contains a certain determinate addition of the foreign metal of the series under consideration. To illustrate the manner of using such a principle, let a series of couples whose constants are known from a calibration between 0° and 350° be in hand; and then let a given fixed temperature (the boiling point of zinc for instance) be determined by each of them. There will be as many values for boiling point as elements. If we regard these as functions of the respective quantities of foreign metal in the negative parts of the couples, and if we represent the calculated boiling points as ordinates, and the percentage compositions of the alloys as abscissæ, we obtain a locus the nature of which may be sufficiently obvious to enable us to prolong it as far as the axis Y. The point of intersection, therefore, approaches very closely to the datum of the hypothetical element platinum-platinum.

If the effect of alloying metals were merely that of joining them in multiple arc, the interest which belongs to the problem in hand would at once vanish.

For if e_1 and e_2 be the electromotive forces of two wires thermo electrically combined with platinum, and if w_1 and w_2 be the resistances of these wires, then

$$e=\frac{e_1+e_2\frac{w_1}{w_2}}{1+\frac{w_1}{w_2}}$$

where e is the equivalent electro-motive force. Hence if $r=w_1 \mid w_2$,

$$e=\frac{1}{1+r}\left\{(T-t)(a_1+a_2r)+(T^2-t^2)(b_1+b_2r)\right\}$$

which may be abbreviated

$$e=\frac{1}{C}\left\{A(T-t)+B(T^2-t^2)\right\}.$$

From this it follows that

$$T=\frac{A}{2B}\left(\sqrt{1+e\frac{4BC}{A^2}}-1\right).$$

If in this equation $w_2=\infty$, which supposes this metal to vanish from the alloy, and if additionally a_1 and b_1 be made equal to zero, we arrive at an expression of T in terms of $\frac{0}{0}$. This result shows that however near we may approach the limit couple platinum-platinum, any thermal datum derived by thermo-electric means will none the less be dependent on the properties of the metal combined in multiple arc with platinum.

In the case, however, of metals alloyed, the results are quite different; for here the thermo-electrics of the alloy bear no intelligible or general relation to the ingredient metals of the alloy, so far as our present knowledge goes. Indeed it is not infrequent to find the admixture of an electro-negative ingredient produce a distinctly electro-positive result. And hence it follows that constants referring to the final or infinitely dilute alloy have a special and unique significance. In the final alloy we have one metal combined by fusion with another in such a way as to produce absolutely no variation of molecular arrangement. If, therefore, data for the limit couple be investigated, they are those from which a clue respecting the dependence of the thermo-electrics of the compound upon those of its constituents may most probably be obtained. Table 7 shows the sensitiveness of couples to be frequently such that the final element platinum-platinum may be approached very near, and it is for this purpose largely that the table was drawn up. With the object of basing the discussion on electric data exclusively, the constant a may be taken as a symbol of the composition of the alloy-component of the thermo-couples of a given series; and hence the curves or loci here in question are obtained by representing any fixed datum (for instance the value of the boiling point of zinc which obtains for the special couple under consideration) as a function of a. We have attempted this with the data in hand, but they are not yet in sufficient number to give any definite hints as to the nature of the relations sought. It is necessary, moreover, to confine such work to data obtained from scrupulously pure platinum and from scrupulously pure alloys—conditions which in case of the data of Table 7 are not vouched for. Indeed the table gives evidence of the varied character and purity of platinum derived from different sources and shows a widely different electrical behavior of nominally the same alloys.

There is one respect, however, in which the data of Table 7 are crucial. They show that extrapolations based on the equations of Avenarius and of Tait lead to very different high temperature results. They, therefore, prove that these equations are insufficient, and point out the probable tendency toward an anomalous thermo-electric behavior, to allotropic modification and polymerization even in the most stable alloys.[1] Herefrom it follows that the pyrometric value of any alloy can only be determined by a minute thermo-electric survey made by aid of the air-thermometer, throughout the whole range of variation of thermo-electromotive force and temperature.

Intimately connected with the present discussion are questions relating to the relative variations of *a*, *b*, or even higher constants of the thermo-electric formula. Tidblom (l. c.) has endeavored to throw light on this subject, not without success. If *a* and *b* vanish at the same rate, then the data of the limit couple are as truly intrinsic, i. e., as fully dependent on the metals of the series to which the couple belongs, as any other. But if *b* vanish at a rate which is relatively very rapid as regards *a*, then the thermo-electric equation becomes ultimately linear. Extrapolations made by aid of the limit couple will therefore be more justifiable in proportion as the fraction $\frac{b}{a}$ tends toward zero.

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[1] Cf. Le Chatelier, loc. cit. Our own results (see Table 6) were completed in 1884, but in consequence of delays in moving the laboratory, publication was delayed (see Preface).

CHAPTER II.

THE CALIBRATION OF ELECTRICAL PYROMETERS BY THE AID OF FIXED THERMAL DATA.

EXPLANATION.

In the apparatus described in the foregoing chapter, great masses of metal were kept at the boiling point. The advantages gained from a brisk but perfectly free circulation of vapor, particularly in the case where the vapor is of small specific heat, have already been pointed out. It is to the use of large apparatus that Messrs. Deville and Troost had been led before us. In their experiments, however, the direct use of the air-thermometer made a boiler of considerable size essential from the outset.

Large and expensive apparatus, whatever be their special advantages, can never enjoy extensive use in the general laboratory. It is therefore the object of the present chapter to describe special forms of apparatus by which calibrations of thermo-elements may be quickly and safely made, and by which the problem of thermo-electric temperature measurement may be reduced to an ordinary laboratory experiment.[1] The degree of error to which the observer is liable, the degree of constant temperature attained, the selection of substances having convenient boiling points, and finally the application of the apparatus to a variety of substances for boiling-point measurement will constitute the chief topics of this chapter. The boiling-point apparatus must of course be such that ebullition may be kept up indefinitely.

APPARATUS FOR LOW BOILING POINTS (100° TO 500°).

Original forms of boiling-point tube.—The original forms of boiling-point apparatus for mercury, for sulphur, and for aniline, water, etc., are given in Figs. 7, 8, 9, drawn to a scale of ½. They are all constructed on essentially the same principle, slight modifications being introduced to meet each case. The apparatus, Fig. 7, consists of an ordinary glass lamp chimney, *aaaa*, inverted as shown, and closed at its lower end by a plaster of Paris plug, *bb*, surrounded by a wrought-iron cap, *cc*. The cap *cc* is larger than the glass, and by pouring in the plaster in the moist condition and allowing it to set, the tube is firmly secured between

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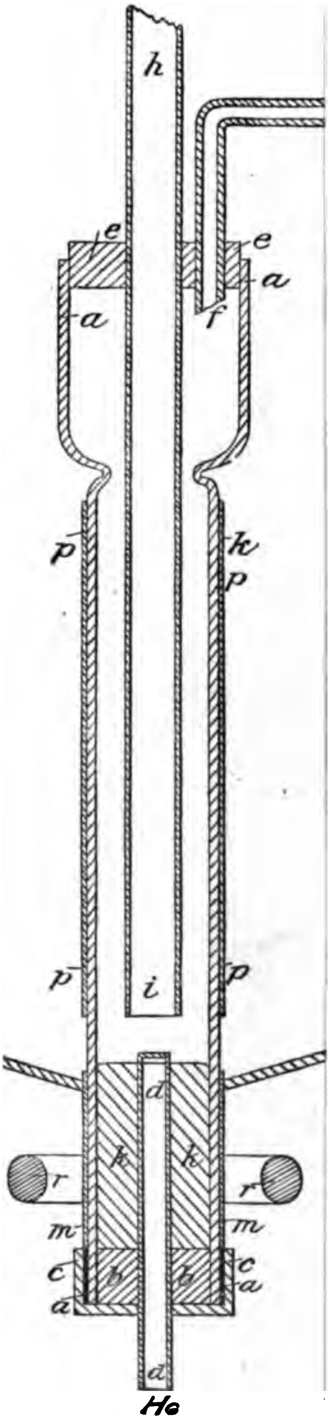
[1] Since the completion of the work of the present chapter, M. Le Chatelier has made pyrometric experiments with ends in view similar to those here proposed. (Cf. p. 50.)

Fig. 7.



Figs. 7, 8, and 9.-

the body of plaster within and a layer of plaster braced against the iron cap without. The cap *cc* carries an iron tube, *dd*, closed above but open below, and occupying a central or axial position with respect to the glass tube, into which it projects about two inches clear. The top of the lamp-chimney is closed by a suitable cork, *ee*, doubly perforated, through the central hole of which is inserted a wide glass tube, *hi*, partially closed above by a loosely fitting stopper. Through the other perforation passes a glass tube, *fg*, by aid of which some gas (N_2, CO_2) may be introduced. The glass *aaaa* is partially filled with the substance whose boiling point is to be used (in the present instance mercury), only enough being poured in to submerge the central tube *dd* with the exception of about 0.5^{cm} of its head. To keep the metal in ebullition, use is made of Dr. Wolcott Gibbs's ring-burner,[1] *rr*, the flame of which is properly regulated. Very thin copper or brass gauze, or copper-foil, *m m*, surrounding the part of the glass tube encircled by the ring-burner, is sufficient to almost completely obviate the dangers of breakage; and a circular screen of thick asbestos, *n n*, bent in the shape of an inverted cone protects the top of the tube *dd* from direct radiation. Above *nn* it is well to surround the tube *aaaa* with a thick jacket of asbestos, *pppp*, extending as far down as may be without shutting the surface of boiling mercury entirely out from view. The mercury which condenses on the sides of the tube falls back in small drops into the mass *kk* below. The process is therefore continuous.

The properly insulated thermo-couple is introduced into *d d* from below, and the hot junction is pushed forward quite as far as the top of the tube *d d* and slightly above the surrounding surface of mercury. A screen may be fastened a little below the cap *c c* to shut off all radiation from the cold junction, which is submerged in oil.

The apparatus for sulphur in Fig. 8 differs from that in Fig. 7 only in that the wide central tube *h h i i* has within it a second glass tube, *q t*, partially closed above with a cork. This second tube whenever the passage below is stopped up by the distillation of sulphur may be at once removed and a similar clear tube inserted. A slow current of dry carbonic acid gas entering at *g* passes through the apparatus during ebullition. Subsequent experiments showed that with suitable changes in the apparatus the tube *h h i i* as well as gas current could be dispensed with. This will be referred to again below. The sulphur condenses on the sides of the tubes and by far the greater part runs back into the mass *k k* below. There is a line of demarkation encircling the tube where the temperature is the melting point of sulphur.

For liquids with a boiling point below that of mercury and sufficiently low not to char a cork, the boiling tube may be considerably simplified in the way shown in Fig. 9. Here both ends of the lamp-chimney are closed with a cork centrally perforated to admit a long glass tube, *d d*,

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[1] The Gibbs ring-burners were introduced into this laboratory by Drs. Gooch and Chatard, and have since become invaluable.

extending quite through the tube *a a a a* and open at both ends. The tube *d d* is wide enough to admit a mercury thermometer at its upper end, held in place by a cork, *g*, secured by an end of rubber tubing. The lateral tube of the upper cork *e e* is here somewhat wide and long, its object being to allow of the escape of vapor, should this be necessary. By suitably regulating the flame of the ring burner, however, the heat applied may easily be made such that the vapor condenses near the middle of the tube *f g* and returns to the liquid below. Thus the process is again continuous. A sharp line of demarkation around the tube *f g* shows the part of it where the temperature is just low enough for the condensation of the liquid used.

Many experiments were made with each of these three forms of apparatus, the results of which will be more appropriately given below in connection with other similar experiments.

Perfected form of boiling tube.—The three forms of apparatus for low temperature just described, each of which contains certain special desiderata, can be combined into a single form adapted to the divers cases specified. This final form is given in Fig. 10, scale $\frac{1}{4}$. The glass parts were made for me by Messrs. Whitall, Tatum & Co., in Philadelphia. Special care is of course to be taken to have the tubes well annealed. As the lettering of Fig. 10 is identical with that of Figs. 7 to 9, only a few additional words of explanation are necessary. The tube *a a a a* is completely closed above by the cork *e e*, and communication with the atmosphere is effected by the bent glass tube *h i*, ending in a little vessel, *g*, open below and filled with asbestos wool. The tube *g* is a filter, catching noxious mercurial fumes should any such escape. It also impedes entrance of air when the boiling tube is filled with some other gas. The central tube *d d* is closed, of course, either with a perforated cork carrying a mercury thermometer, or at higher temperatures with asbestos wicking pushed downward into the tube almost as far as the point *o* of the thermocouple. The position of the thermo-couple *o* α and *o* β is pretty well represented, the two wires being held apart by a doubly perforated insulator, *o y*, of porcelain or of fire-clay. The clamp attached to the lower end of the tube *d*, which holds the insulator *o y* in position, is easily imagined, and is therefore omitted in the figure. When the screen *n n* fits snugly it remains in place of its own accord, or it may be wired to the gauze covering *m m*. The boiling-tube *a a* and the burner *r r* being each supported by an ordinary retort holder with universal clamps, are easily adjustable at pleasure.

In the case of substances which are spontaneously inflammable at their boiling points, like sulphur, the oxygen of the tube is so soon exhausted that ebullition takes place without interruption. Hence the introduction of special gases like N_2 or CO_2 is rarely necessary; a great advantage, inasmuch as the introduction of gas, no matter how slowly or how regularly, always interferes with the constancy of temperature. In case of mercury, however, the metal must be renewed from time to time, otherwise the ebullition, which is regular in the case of pure metal, becomes irregular and bumping when it holds perceptible quantities of oxide in solution, or when such adhere to the glass. Solids may be either melted and poured into the tube from above, or they may be introduced as powders and then cautiously melted. In case of organic solids heat must be applied very gradually to prevent charring or gumming, until the whole mass is liquefied. Usually the substance may be left to cool and solidify in the tube without incurring liability to breakage, a special tube being set apart for each boiling-point substance.

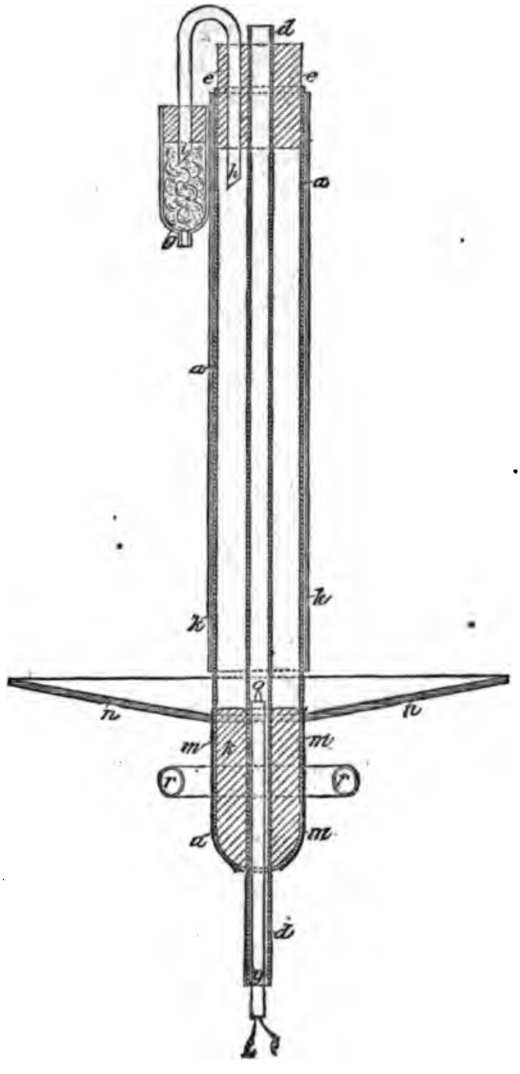

FIG. 10. Perfected form of boiling-tube. Scale, ½.

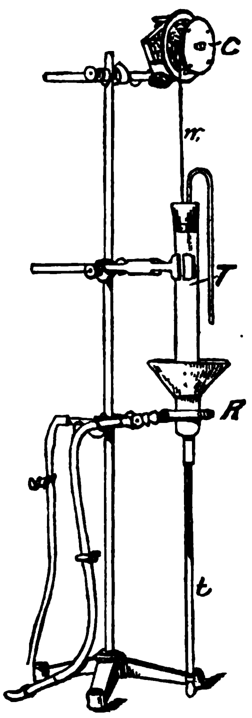

FIG. 10a. Boiling-point tube for annealing long wires. Scale, $\frac{1}{10}$.

If the thermo-element is removed and the lower end of the tube *d d* is prolonged downward by fastening on to it with a piece of rubber hose a similar glass tube, *t*, Fig. 10, closed below, these boiling tubes are obviously well adapted for annealing long wires of steel or metal, for magnetic or other purposes. Such wires are drawn regularly through the hot zone by clock-work;[1] a drum, *C*, taking the place of the hour hand, from which drum the wires to be annealed are suspended by a very fine copper wire, *w*. This method I have frequently used with success.

Boiling-point tubes for pressure work.—When it is desirable to boil substances under pressure greater or less than one atmosphere, a form

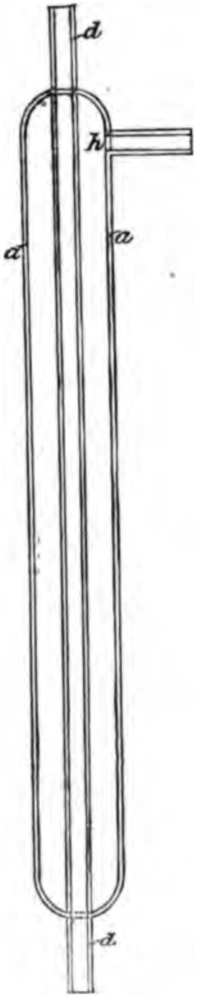

FIG. 11. Boiling-point tube for pressure work. Scale, $\frac{1}{3}$.

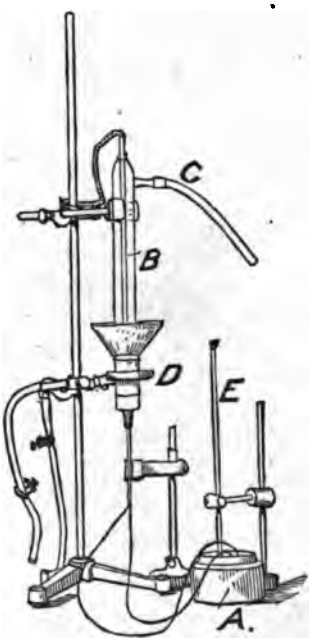

FIG. 11*a*. Boiling-tube for pressure work, with accessories. Scale, $\frac{1}{10}$.

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[1] Cf. Am. Jour. Sci., 3d series, vol. 32, 1886, p. 279.

of tube shown in Fig. 11 is convenient. This differs from the other forms only inasmuch as the outer tube *a a* is closed upon the central tube *d d* both above and below. A special lateral tubulure, *h*, communicating with a manometric arrangement subserves the purpose of varying the pressure by any amount compatible with the strength of the tubes. It is also through *h* that the substance to be boiled is introduced. It is by means of this arrangement, that I purpose to study the relation between boiling point and pressure over long ranges, and for mercury, sulphur, and divers other substances. The thermo-element for such purpose must be calibrated with the re-entrant glass air-thermometer described in Chapter IV.

Tubes of this kind I obtained from M. Emil Greiner, of Nassau street, New York. Glass of a specially hard quality is made by Appert frères, Clichy, France. Inasmuch as M. Troost was able to boil selenium in this material with impunity, the upper thermal limit of the glass boiling tube may be considered given by the boiling point of selenium. Tubes of the kind here described for investigating the boiling-point pressure functionality are the simplest and at the same time the most

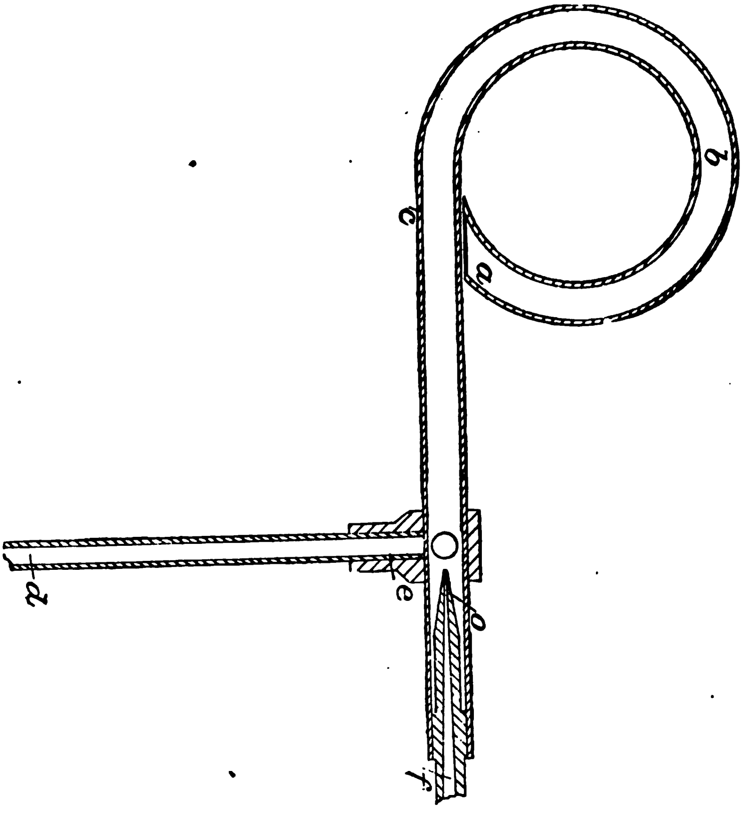

FIG. 12. Ring-burner. Scale, ½.

accurate forms yet devised. The completed adjustment is well shown in Fig. 11*a*, where *B* is the boiling tube, *R* the ring burner, *A* the oil bath for the cold junction of the thermo-couple, *E* the thermometer of the cold junction. The central tube is closed by a piece of asbestos wicking, as shown. Communication with the air-pump takes place through *C*. Mr. Greiner has since succeeded in inserting a second tubulure in the top of the boiling tube, Fig. 11, through which a mercury thermometer may be inserted, thus affording additional means of thermal comparison.

Dr. Gibbs's ring-burner.—A final reference is to be made to the ring-burner. This is shown diagrammatically about one-half full size in Fig. 12. The burner proper, *a b c*, is a circularly bent tube of brass or iron, on the inner side of which about forty radially disposed holes, each about 0.1^{cm} in diameter, have been drilled. The straight tube *c f* connects the ring with the injector, the tube *d e* admitting of the influx of gas, the tube *f o* of the injection of air. Both the tubes *d e* and *f o* are provided with stop-cocks. Where only moderate intensity of flame is desirable gas may be passed in at *f* and the tube *d e* left open. Either of the tubes *d e* or *c f* is available for clamping the burner in the ring stand. In the general case where a blast is necessary Professor Richards' pneumatic injector is most easily applicable. The pump which can be used equally well either for slight compressions or for exhaustions is now in such general laboratory use that special description is unnecessary.

It is probable that for special purposes boiling tubes of larger diameter will be preferable, but such tubes are more fragile and the manipulation is of necessity less expeditious.

APPARATUS FOR HIGH BOILING POINTS.

Original forms of boiling crucible.—The tubes just described are no longer convenient when the boiling point of the substance exceeds low redness. In such a case bellows have to be used for injecting air and the glass tube itself, becoming more and more viscous, yields gradually to the charge of metal it contains. Hence for high temperatures it is necessary to replace the glass tube by crucibles of fire-clay or of porcelain. In Fig. 13 I have given the original form of an apparatus of this kind. It consists essentially of two French crucibles, *a a a a* and *b b b b*, put together on the flat open end, which it is well to grind smooth. Both crucibles are perforated. A porcelain tube, *d d*, has been cemented into the lower crucible with asbestos cement. This tube, closed above, open below, and glazed exteriorly, is to contain the thermo-element. Through the tube *g h* above, some reducing gas, notably hydrogen, may be introduced, the tube *g h* being either glass or porcelain. The lower crucible is partially filled by the metal or other substance, *k k*, whose boiling point is to be used, care being taken to introduce no more than is just necessary to cover the central tube *d d*. The lower crucible is surrounded by a furnace, *F F F F*, made of the same non-conducting mixture which is used in Fletcher's small injector furnace. Heat is communicated by means of the injector blow-pipe *A B C*, gas entering at the tube *C*, air at *E*. Both *C* and *E* are provided with stop-cocks. The products of combustion escape at *D*. The crucible *a a a a* has been fitted into the bottom of *F F*, through which the central tube *d d* projects. All cracks and crevices are closed up with carded asbestos. In this way the space below the furnace remains practically cold and the thermo-element may be inserted or withdrawn with great convenience. A few screens protect the cold junction from radiation altogether.

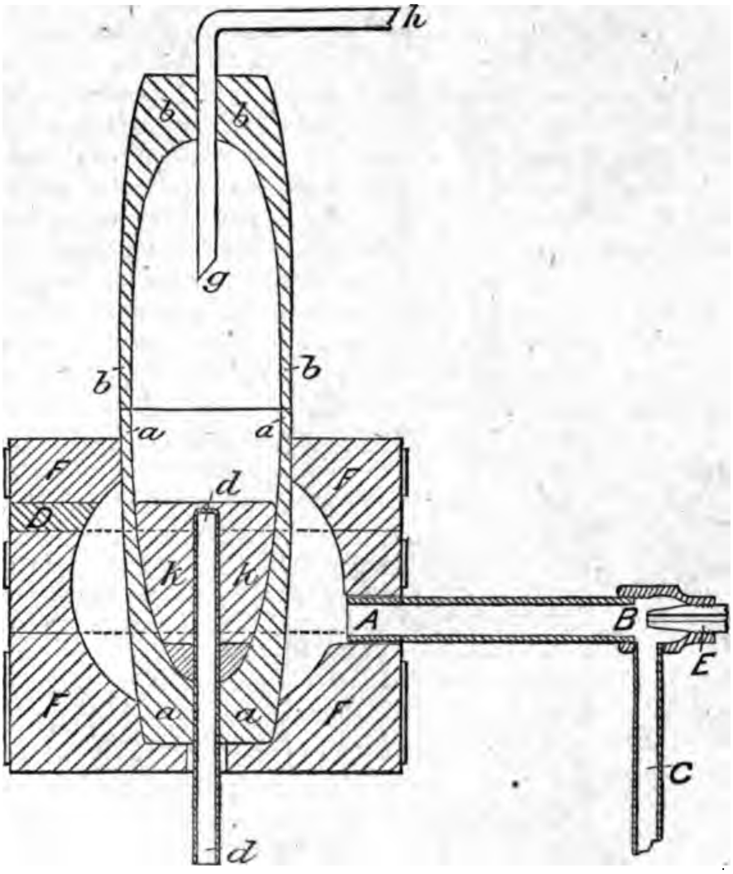

FIG. 13. Original form of boiling crucible. Scale, ½.

Perfected forms of boiling-point crucible.—This double crucible apparatus behaves excellently until the extreme white heats are reached, after which the porcelain and the cement become viscous, and leakage and failure of the experiment is the invariable result. Moreover, the influx of cold hydrogen is not unobjectionable, and it is probable that by using closed forms H_2 may be dispensed with. I was fortunate, therefore, in obtaining crucibles of fire-clay from Messrs. Hall & Son, made in such a way that both crucible and central tube are one single piece. A crucible of this kind is shown in place in Fig. 14, in which the parts have been numbered similarly to Fig. 13. A conical shape is here given to the crucible, with the object of decreasing the essential charge of zinc and of thereby expediting the boiling. The furnace-body *F F* and lid *F′ F′* are both properly bound with iron, as shown at *mm*, *mm*, *mm*, and the body rests on a bed-plate of iron, *z z*, provided with a hole through which the botttom of the crucible *a a* partly projects. *Z Z* is raised on rather tall legs, allowing the operator to manipulate the thermo-elements from below. The crucible projects above the furnace, and the lid *b b* is shouldered. A battery of three or four of these fur-

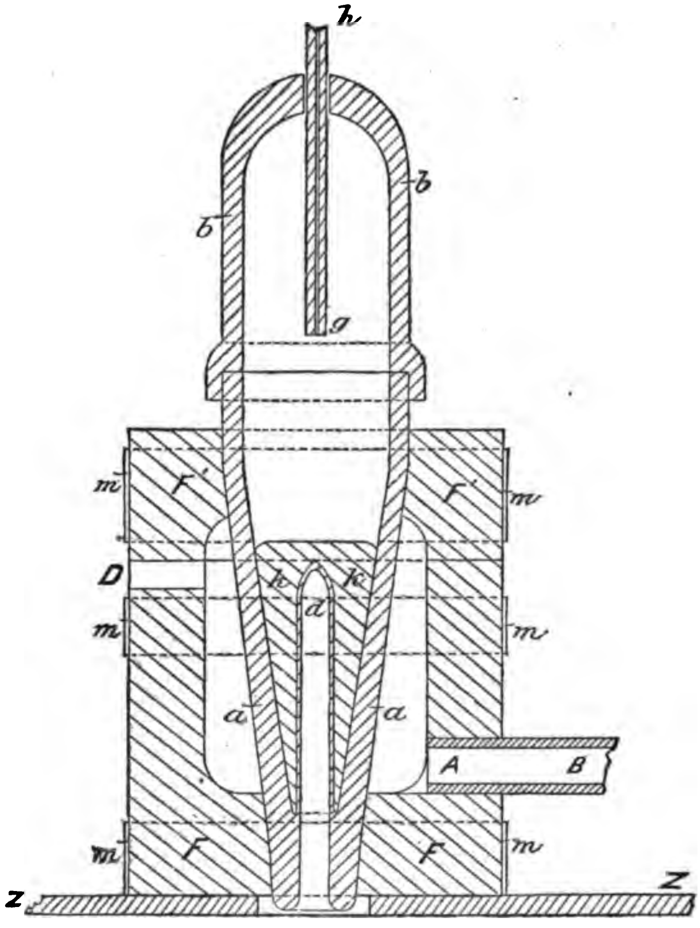

FIG. 14. Perfected form of boiling-point crucible. Scale, ½.

naces may be placed on the same bed-plate, in a row. Each furnace is provided with its own burner, all of which are fed from the same bellows and the same gas-supply (see frontispiece under *D*). It is best for this purpose to attach the bellows (Fletcher's pattern) to an engine, on a very short crank. The pressure of air may then be regulated by increasing the length of the crank. Burners constructed on the plan described at length below (page 183), only on a smaller scale, are preferable. They do not explode back. For very high temperatures two and even three such burners may be made to impinge on the same crucible. For cadmium or zinc a single burner is more than sufficient. At high temperatures the efflux hole *D* may be partially closed with asbestos. The products of combustion escape uniformly on all sides around the plane where the furnace-body and furnace-lid meet. A ring of asbestos, placed around the crucible to protect it from the flame of the burner, is soon fluxed down upon it, and is apt tc destroy the crucible. A ring of baked fire-clay, however, is good.

The crucible shown in Fig. 14*a* is intended for work in which the variations of boiling point and pressure are to be investigated. It is made of refractory porcelain and glazed within. The lid *c a b* fits pretty snugly into the crucible *c f d*, so that the two may be sealed hermetically at the joint *c d* by sodium tungstate (Gooch) or other material. The tube at *a* is in connection with the air-pump. Such crucibles are available for the ebullition of salts of selenium, cadmium, zinc, and probably antimony and bismuth in vacuum. Being made of porcelain they can be more elegantly shaped than fire-clay crucibles, but they become seriously viscous at a lower temperature.

A second form of boiling crucible is shown in Fig. 15. It differs from Fig. 14 only in this respect, that the central tube *d d*, which in Fig. 14 is closed just below the surface of the boiling metal, in Fig. 15 extends quite through the crucible and out of the top. The latter form has the advantage that the degree of constancy of temperature along the length of the tube may be explored by inserting an insulated thermo-element. The part of this tube above the surface of ebullition is closed during the measurement with a fire clay plug, and at the top with asbestos wicking. The form shown in Fig. 15 may also be used for annealing wires at definite high temperatures, by drawing them through the zone of ebullition by clock-work (cf. Fig. 10*a*). This form has therefore many decided advantages over that in Fig. 14, with the one serious disadvantage of being much more fragile. Fortunately it appears from the data below, that the more practical form, Fig. 14, is quite reliable as regards accurate value of the boiling points attained.

In all cases the substance to be boiled, *k k*, must surround the tubes *d d* below the plane of the burners, even more than has been shown in Fig. 14. When this is the case no part of the tube *d d* will be at a temperature higher than the boiling point of *k k*, a desideratum.

In case of Zn, Cd, and other metals the crucible must be glazed internally either with borax, or with silicate of soda or with some fusible porcelain glazing, otherwise the vapors at once permeate the central tube *d d* and corrode the thermo-element within. The presence of vapor may be discovered by inserting a porcelain pipe-stem into *d d* and rapidly withdrawing it. Metallic vapor, if present, usually coats the white stick with a black metallic covering, which rapidly oxidizes. Bi, Sb, Sn, Pb, etc., glaze the interior of the crucible in virtue of the fluxing power of their oxides. This corrosive action eventually becomes sufficiently active to eat its way through the central tube and discharge the contents through the bottom.

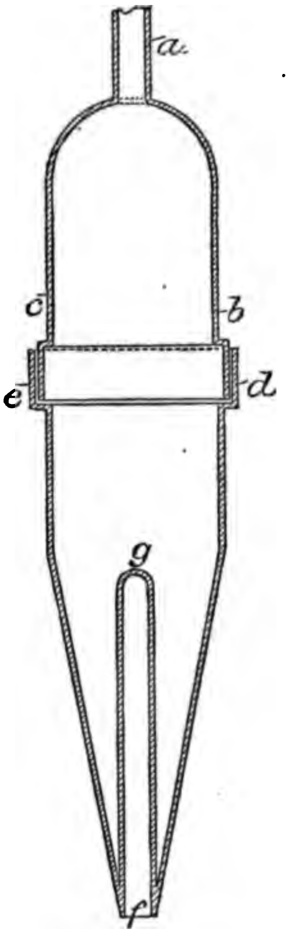

FIG. 14*a*. Boiling-point crucible for pressure work. Scale, ½.

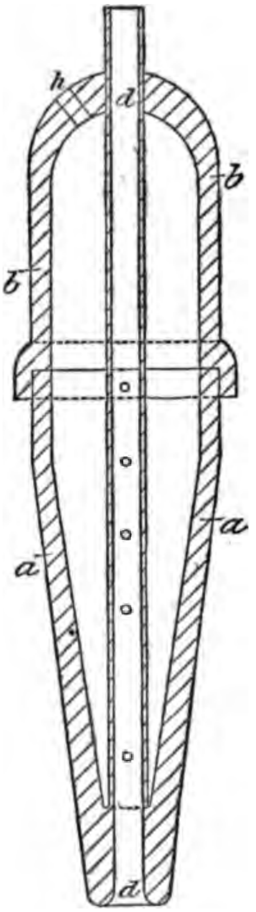

FIG. 15. Boiling-point crucible, open tube. Scale, ½.

A single crucible seldom will stand more than one ebullition, but a single ebullition may be prolonged many hours. If a zinc crucible be broken open when cold the walls are found to be covered with a coating of metal consisting of solidified drops of zinc, which were distilled, recondensed, and ran back again down the sides. In the same way the central tube is kept covered with a coating of zinc. Zinc dust escapes at the joint between lid and crucible, and eventually melts, forming an impervious joint. Zinc dust also escapes where the hydrogen tube enters the lid. In case of zinc and cadmium, this is an excellent criterion of ebullition. In all cases the burners are to be shut off until the escape of metallic dust at *h* is only just apparent. Metals like Sb, Bi, have no such boiling-point criteria, and whether or not the metal has boiled becomes a matter of conjecture. Tin charges slag so heavily that the metal is soon jacketed with a thick viscous coat and the state of the metal under it can not be known.[1]

INSULATORS.

A very essential part of the thermo-element is the insulator. The device which after very many trials I finally adopted therefore deserves careful description here. These insulators are thin stems (0.45^{cm} in diameter, or larger), containing two parallel canals, as far apart (0.20^{cm}) as possible, and about 0.1^{cm} in diameter each. In order that these stems may be of value, they must be made in a way which affords a perfect guaranty that throughout the length of the insulator the canals nowhere coalesce. The following machine, Figs. 16, 17, by aid of which insulators of almost any diameter and with any number of holes or canals may be made in lengths of 25^{cm} to 30^{cm} or more, gives full warrant to this assumption. The tubes are simply pressed after the well-known manner used in the manufacture of lead pipe.

In Fig. 16 (scale $\frac{1}{4}$) *A B* is a thick scantling of wood, fastened vertically, to which a short cross-scantling, *C*, is firmly braced by bolting two boards, shaped as in the figure laterally against both *A B* and *B C*. *B C* carries a barrel of strong gas-pipe, *a a a a*, out of which the porcelain is to be pressed. To secure *a a a a* the piece *C* has been cut apart in the middle parallel to the plane of the paper, and the hole for the barrel is somewhat scant. Hence when the two halves of *C* are drawn together by a couple of strong bolts the barrel is almost immovably fixed. The barrel is surmounted by a cap, *c c*, through which passes a piston or plunger, *d e*, which can be moved up and down by the handle *f g* in the way which the figure readily shows. The lower end of the barrel is closed by the die-cap *h h*. A lateral hole, *b*, allows of the introduction of porcelain or fire-clay slip until the barrel is quite filled. Downward motion of the plunger forces the slip through the

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[1] Experiments since made with the crucibles, Fig. 14*a*, showed that the vacuum boiling point of Bi is easily reached. To get a tight joint at *e d*, the space between lid and crucible is first calked with fibrous asbestos. A ring of fusible metal is then poured upon it. This melts at high temperatures; but when the joint is well made, it is not forced through into the crucible. In future experiments I purpose to have the whole crucible made in a single piece. Cf. Preface.

die, the construction of which is as follows: A narrow but strong arch[1] of brass, *i i*, carries two steel needles, *n*, which project symmetrically into and through the brass tube *k*. It is obvious that the slip, on being forced around the arch and needles, issues from the tube *k* as a biperforated tube, the dimensions of which, either as to external diameter or diameter of canals, depends solely on the thickness of the needles and width of the tube *k* selected, and can therefore be varied at pleasure. It is also obvious that the number of canals is immaterial so far as the application of method is concerned. Fig. 17 (scale ½) gives the die for making the fine porcelain tubing used in the crucibles, Fig. 13, above.

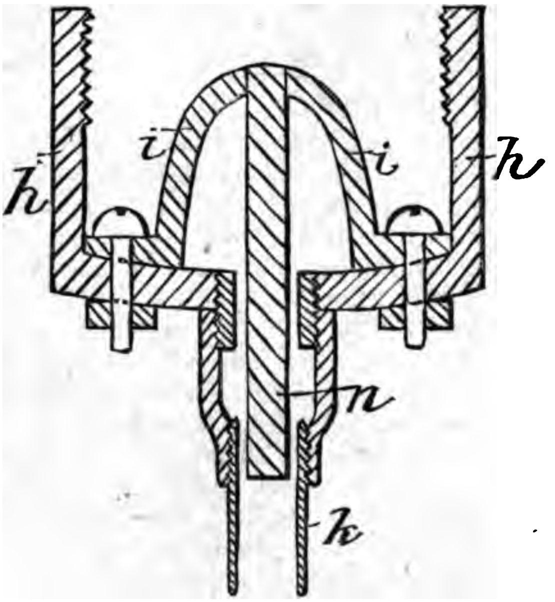

Fig. 17. Die for porcelain tubes. Scale, ½.

When the slip is of proper consistency the tubes issue from the die in a single length so long as the pressure of the plunger continues. Tubes longer than a foot, however, break by their own weight if suspended wet. Hence it is desirable to cut them off by a thin rectangular pine board of about 1 foot in length, held with its long edges nearly vertical and its plane also slightly oblique to the vertical. A great number of consecutive lengths of 1 foot may be laid side by side in this way, like the bars of a gridiron, and then allowed to dry on the board before firing. Insulators of porcelain are smooth and compact, but they become viscous and are even apt to fuse at higher temperatures. Under these circumstances they not only stick to the central tubes of

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[1] The brass arch, *i i*, to hold the pins *n*, was suggested to me by Doctor Hallock. In my original apparatus the pins were fastened to the plunger.

the crucibles (Figs. 13, 14, 15), but they become electrically conducting and are objectionable. Insulators of fire clay are therefore preferable, inasmuch as they are at least as refractory as the crucibles, and Messrs. Hall & Sons, of Buffalo, to whom I sent the above machine, succeeded excellently in making them. Work with fire-clay calls for great experience and skilled manipulation, and it is therefore best to put this work into trained hands. The Buffalo insulators are 25^{cm} to 30^{cm} long. I received two sizes, the larger of which is 0.65^{cm} thick and the smaller only 0.45^{cm} thick. The capillary canals in both cases are slightly less than 0.1^{cm} in diameter. The rods are hard and firm and withstand considerable usage.

METHOD OF MEASUREMENT.

Thermo-element.—A zero method of measurement has been used throughout. All results for thermo-electric force are referred to the Latimer-Clarke, and other standards. This has the advantage of not requiring an iron-free observatory for magnetic work, a desideratum with which I, for instance, had to dispense. The thermo electric use of the zero method was first introduced by Kohlrausch and Ammann.[1] Dr. Strouhal and I introduced certain improvements by which this method can be made to yield results of exceptionally great accuracy. These improvements have been described in Bulletin No. 14, U. S. Geol. Survey, p. 34, but in the interest of completeness it is desirable to recapitulate the chief features of this method here, also to make comparisons of the electromotive force of the hydroelectric standards.

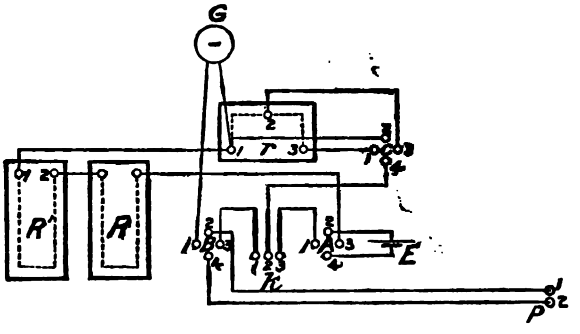

FIG. 18. Disposition of thermo-electric apparatus.

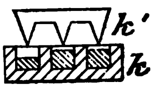

FIG. 19. Double key.

In Fig. 18 a diagram of the connections as actually made with some view to the practical disposition of apparatus is given. In this figure R R^1 are rheostats with 1 to 50,000 ohms available, r a bridge rheostat with pairs of units 0.1, 1, 10, 100, 1,000, and 10,000 ohms available. A and B are commutators, K and C keys. The terminals of the thermocouple communicate respectively with the points P_1 and P_2. This is

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[1] Kohlrausch u. Ammann: Pogg. Ann., vol. 21, 1870, p. 450.

the cold junction of the couple, and to keep P_1 and P_2 at the same temperature they are submerged in petroleum. From P the copper wires pass through the commutator B, and thence one of them passes through the double key K, through a second key, C, to the terminal r_3 of the bridge rheostat r. The other terminal passes through the galvanometer G and thence to r_1. This is the first branch of the zero adjustment, the second branch being furnished by the rheostat r, the ends of which also terminate at r_1 and r_3. Finally the terminals of a pair of zinc sulphate Daniells E pass through the commutator A; from here one terminal passes through the key K and through C to r_3, the other passes through the large rheostats R R_1 and then to r_1, completing the third branch.

When the current is zero in G

$$e=E\frac{r}{R+r}$$

where e is the electro-motive force at e, E the electro-motive force at E in the figure; where R is the resistance at R R', and r the resistance at r in the figure. By means of the key K two circuits conveying currents due to E and e are closed simultaneously. It is, however, essential that they be so closed as to act differentially on the galvanometer G at once. Otherwise there is danger of throwing the needle violently against the stops. Hence in filling the cups of mercury K_1, K_2, K_3 care is taken to keep the level of mercury in K_2 and K_3 decidedly above that in K_1. When the metallic prongs of the key descend to close the circuits, the one not passing through the galvanometer is closed first, and a moment after the differential current passes through G at once. A diagrammatic section through the mercury cups of K is given in Fig. 19. The make-circuit strip K' is of amalgamated copper on a spring which keeps it open against a stop. Circuits may, therefore, be made and broken almost instantaneously. The object of the key C is to enable the observer to use pairs of the resistances of the bridge rheostat r, either in series or in multiple arc. By connecting C_4 and C_1 only, these resistances are used in series; by connecting c_1 and c_2 as well as c_3 and c_4 they are used in multiple arc. The available resistances are thus 0.05, 0.10, 0.20, 0.5, 1.0, 2.0, etc., as far as about 20,000. The fine adjustment is made at R, which is variable in single units whose mean value is always large. Varying r in steps, in this way, greatly facilitates the computation.

The electro-motive force obtained as above is never wholly due to the thermo-element at P_1 P_2 alone. It contains a disturbing electro-motive force ε, resulting from the accidental distribution of temperature, in connections which can not be thermo-electrically identical throughout. For a short period of time (that of an observation) ε may be considered nearly constant, or at least varying linearly. It may therefore be eliminated, very nearly at least, by two commutators, A and B, as Dr.

Strouhal and I have shown.[1] In a series of corresponding positions of these commutators, alternately opposite, the direct measurements would give

$$\frac{+e+\varepsilon}{+E}=a_1;\ \frac{-e+\varepsilon(1+\alpha)}{-E}=a_2;\ \frac{+e+\varepsilon(1+2\alpha)}{+E}=a_3;\ \text{etc.}$$

where an odd number of observations is made. Let M_1 be the mean of the odd right-hand members, and M_2 the mean of the even right-hand members. Then

$$\frac{e}{E}=\frac{1}{2}(M_1+M_2).$$

In the case of small electro-motive forces this elimination is essential.

Standards of electromotive force.—Inasmuch as all measurements are based upon the constancy of the double Daniell E, it is obvious that the value of this electro-motive force will have to be frequently tested. This can be done very simply and with accuracy by replacing the thermo-couple by a Latimer-Clarke or other standard element and proceeding with the measurements as usual. It is to effect this compensation that the rheostat r must have a large resistance, 20,000 ohms, available. For thermo-electric work $r = 0.1$ to 500 ohms suffices. For a similar reason two Daniells are used instead of one. Currents are made only momentarily, and approximate values of r and R are always known. The constancy of my Latimer-Clark's cells has certainly been exemplary, and it was thus easily possible to reduce the Washington results to the older results obtained in New Haven in a way that established the general accordance of data beyond a doubt. In addition to the Latimer-Clark standards, I possessed for comparison a number of siphon Daniells, certain Beetz's dry Daniells, and a special form of normal Daniell of my own which merits description. In this battery it is impossible, correct usage presupposed, for the copper sulphate to contaminate the zinc. Zinc and zinc sulphate, copper and copper sulphate, are kept in separate bottles, and are only in electric contact during the few minutes of measurement. In Fig. 20 the Zn-Zn SO_4 bottle is on the left, the Cu-Cu SO_4 bottle on the right. Each bottle is provided with an h-shaped siphon of glass, the longer shank of which, $a\ b\ c$, is closed above by a rubber cap, a, and below by a cap of parchment paper tied on. The shorter shank d dips into a little vessel, A, containing Zn SO_4 in solution. When not in use the siphon tube is nearly empty. Before using both tubes are rinsed thoroughly with Zn SO_4 solution by compressing and relieving the caps a. When clean they are filled in the same way with the Zn SO_4 of the dish A. After using, both siphons are emptied by working the cap a as usual, and the ends d are closed by special caps (not shown) to prevent evaporation. It is obvious that if the rinsing be properly done Cu SO_4 can not possibly get into the zinc flask to contaminate the metal. Zn therefore remains bright for years.

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[1] Bull. U. S. Geol. Survey, No. 14, p. 35.

Results obtained by comparing divers standard elements from 1883 to 1888 are given in the next tables. Unfortunately time-magnetic measurements are not feasible in our laboratory, with a degree of certainty to warrant their adoption. Nevertheless by comparing Latimer-Clark and Daniell standards, the respective tendencies to variation of which are probably of an opposite character, some corroborative information may be obtained. In the next table the time or date of comparison is given in the first column. The next five columns contain data for Latimer-Clark elements, of which Nos. *D*, *E*, *F* were made by myself. Nos. 114 and 115 are Elliott standards. Curiously enough, the latter are neither as rigorously constant, nor is their internal resistance as small relatively as is the case in my own standards. I have reason to believe that one or both of the Elliott standards suffered by transportation, for in the examination made in 1887 No. 115 was found entirely out of order and was necessarily discarded. In the siphon Daniells the two jars are like those in Fig. 20, except in so far as they are permanently joined by a siphon. This siphon is filled with zinc sulphate through a small vertical tubulure during use, and emptied after using. With all precautions, however, it is impossible to keep the copper sulphate from diffusing into the zinc jar and corroding the metal. Hence this siphon form is inferior in efficiency to the separate cell form *Q* already described. Beetz standards[1] are also made by myself. Electromotive forces are given in volts.

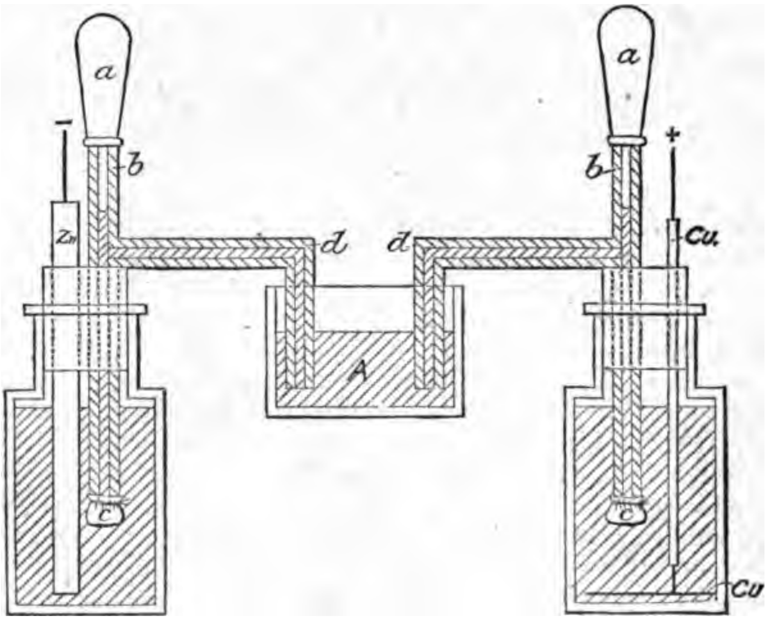

FIG. 20. Standard Daniell. Scale, ¼.

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[1] Wiedemann Ann., vol. 23, 1884, p. 402.

TABLE 9.—*Comparison of standard elements.*

[All values reduced to 20° C.]

Date.	Latimer-Clark standards.					Standard Daniell cells.							Temperature.
						Siphon-joined cells.			Separate cells.	Beetz gypsum cells.			
	D.	*E.*	*F.*	Elliott, 114.	Elliott, 115.	*G.*	*H.*	*I.*	*Q.*	*g.*	*h.*	*i.*	
Dec. 18, 1883	1.420	1.420	1.420	....	....	(1.056)	......	......	......	.....	......	......	(*)
Jan. 2, 1884	1.420	1.420	1.420	....	....	1.050	1.050	1.052	......	......	......	......	†14°
Oct. 26, 1885	1.420	1.426	1.426	1.384	1.403	......	......	......	......	1.083	1.083	1.081	‡19°
Mar. 22, 1886	1.420	1.427	1.426	1.371	1.306	1.076	......	......	1.074	1.022	1.037	1.013	§20°
Aug. 13, 1887	1.420	1.428	1.430	1.350	....	1.079	......	......	1.075	1.030	1.024	......	28°

* Immediately after making the Latimer-Clark elements D, E, F.
† Immediately after making the Daniell G, H, I.
‡ Immediately after receiving the Elliott standards.
§ Immediately after making the Daniell Q.

In the construction of this table the element *D* is assumed to be constant, and with this premise the data of the table are at once intelligible. I need only remark that my Latimer-Clark standards, as compared with the separate-celled Daniell *Q* during the seventeen months of observation, are as good as absolutely constant. It is for this reason that I am warranted in placing much confidence in the data of both these couples, of which the Daniell has the advantage of constancy and the disadvantage of less facile manipulation. The siphon Daniells are inferior to the form *Q*, as are also the Beetz patterns, concerning which, however, it is necessary to remark that the gypsum mixture of copper sulphate and zinc sulphate solutions were probably too moist. I found after a time that the line of demarkation had disappeared and that the solutions must have diffused into each other.

It will be seen that the elements *D*, *E*, *F*, though identical among themselves, differ considerably from Elliott's Latimer-Clark's; not more so, however, than Elliott's elements differ among themselves. A much more curious result was obtained in measuring the temperature coefficients of the siphon Daniell's and the Latimer Clarke's. To do this the elements were first covered with melting snow and afterwards submerged in water heated to different temperatures. Measurements were made by the zero method described, and to give additional certainty an auxiliary Daniell was used for comparison. In other words, the elements *g*, *h*, *i*, *E*, *F*, heated to the temperature specified, were compared with *D* and *B* kept cold, by inserting them alternately in the same connections; *D* was compared by a galvanometer method. The main comparisons were made in 1883, certain corroborative data added in 1887. α is a mean constant, derived graphically and intended for practical reductions only. Electromotive forces are given in volts.

Taple 10.—*Temperature variations of the Latimer-Clark standards D, E, F.*

1883.

t.	Standard No. *E.*		Standard No. *F.*		Standard No. *D.*		*a* Mean temperature coefficient of *D, E, F.*
	E.	Check Daniell at 20°.	*E.*	Check Daniell at 20°.	*t.*	*E.*	
0	1.424	1.072	1.425	1.072	0	1.422	Between 0° and 40°.
14	1.421	1.072	1.420	1.072	15	1.420	
17	1.420	1.072	1.421	1.072	29	1.415	*a*=−0.00020.
21	1.419	1.072	1.419	1.072	40	1.409	
27	1.417	1.072	1.417	1.072	....	....	
36	1.414	1.072	1.414	1.072	....	....	
41	1.411	1.072	1.411	1.072	0	1.425	Later and earlier data.
48	1.407	1.072	1.407	1.072	10	1.423	
54	1.404	1.072	1.404	1.072	13	1.421	
60	1.400	1.072	1.400	1.072	....	....	

1887.

t.	*E.*	Check Daniell at 20°.	*E.*	Check Daniell at 20°.	*t.*	*E.*	*a*
0	1.439	1.076	1.430	1.076	....	....	Between 0° and 30°.
27	1.426	1.075	1.428	1.074	....	....	*a*=−0.00023.

Table 11.—*Temperature variations of the siphon Daniell standards.*

1883.

No. *G.*		No. *H.*		No. *I.*		*a* Mean temperature coefficient of *G, H, I.*
t.	*E.*	*t.*	*E.*	*t.*	*E.*	
0	1.067	0	1.066	0	1.069	
14	1.072	14	1.072	14	1.073	Between 0° and 30°.
15	1.072	15	1.069	15	1.073	
15	1.072	15	1.071	15	1.073	*a*=+0.00021.
24	1.072	24	1.072	24	1.074	
33	1.074	33	1.074	33	1.076	
44	1.075	43	1.074	43	1.075	
50	1.075	51	1.072	51	1.075	

The electromotive force and temperature coefficient of the Latimer-Clark standard has been much discussed. Besides Clark's[1] original investigation, v. Ettinghausen,[2] who cites the relevant researches (Clark, Helmholtz, Kittler, Uppenborn, Alder Wright) and Rayleigh[3] have given it critical study. My own temperature coefficient is smaller than that ordinarily given, and indeed so small as usually to be negligible. The

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[1] Clark: Jour. Soc. Tel. Engineers, vol. 7, 1878, p. 53.

[2] v. Ettinghausen: Wiener Zeitschr. f. Electrotech., 1884, p. 1.

[3] Rayleigh: Rept. 54th Meeting Brit. Assoc., Adv. Sci., 1884, p. 651; Proc. Royal Soc., London, vol. 40, 1886, p. 79.

cause of this variation may be sought for in the composition of the mixtures. I have, moreover, kept the paste wet with a layer of zinc sulphate, in this way decreasing the internal resistance. In the case of zero work, standards with enormous internal resistances are undesirable, because all necessary resistance is introduced by the rheostats. I made a number of experiments to study the dangers due to polarization in the batteries, and it is the outcome of this work that the large resistances in the connections have been retained. The data themselves are superfluous here.

METHOD OF COMPUTATION.

Many experiments go to show that the quadratic relation

$$e=a\,(T-t)+b\,(T^2-t^2),$$

where e is the electro-motive force for the temperatures T and t of the junctions of the thermo-element and a and b are constants, is a very complete interpolative equation, so long as the temperature T is not too far above red heat. In general, however, it is desirable to express e graphically for each element. The method of measuring e has just been indicated. T is the temperature given either by some known high boiling point or by direct evaluation with the air-thermometer, while t is directly read off by a mercury thermometer. If the graphic chart thus obtainable is subsequently to be used for temperature measurement, it is desirable to refer all values of e to e_{20}, i. e., to the electromotive force which obtains when the hot junction is at T°, the cold junction at 20°. This correction follows easily from equation (1), for if

$$\begin{aligned} e &= a\,(T-t)\ +b\,(T^2-t^2), \qquad \text{and}\\ e_{20} &= a\,(T-20)+b\,(T^2-20^2), \end{aligned}$$

$$e_{20}-e=a\ \ (t-20)+b\ \ (t^2-400).$$

The constant a and b may be determined from the steam and mercury vapor calibration. A table is then to be constructed for the correction $e_{20}-e$ as varying with t. By adding this to any given value of e the temperature results are at once comparable with the values of the chart, in which e is represented as a function of T. t should of course be kept as near 20° as possible.

In the measurement of e, a small table in which the log r is once for all inserted for each r, and another in which the log E is inserted for each R, greatly expedite the computations.

My original plan of calculating the constants of e as a function of T and t by the method of least squares was soon abandoned. These constants do not represent the function truly, and since many calibrations are to be made the computation becomes excessively laborious. Finally, T can be taken from the interpolation chart quite as accurately as it can be measured and with much less liability to error. If equation (1) be solved with reference to T it follows that—

$$T=\left(\sqrt{1+\varepsilon\frac{4b}{a^2}}-1\right)\frac{a}{2b},$$

where

$$\varepsilon=e+at+bt^2.$$

When many values of T are thus to be found the computation is by no means unlaborious.

By keeping r constant, and varying R, a table can be calculated once for all, for the function

$$E\frac{r}{R+r},$$

in which a mean value is inserted for E. Such a table for frequently recurring values of the arbitrary constant r and for values of R, increasing in arithmetical progression with a difference of 1,000, is of great service in facilitating the calculation of e. It insures greater exemption from error. A small correction for E is only necessary to correct the interpolated results.

Instead of applying a zero method like the present, it is of course permissible to use simplified processes in which currents only are measured. A torsion galvanometer, such, for instance, as that actually used by Schinz (l. c., p. 49), suggests itself. By the aid of my boiling tubes and crucibles the scale of such an instrument may be at once graduated in terms of the centigrade thermometer. Not only can this be done with a great degree of accuracy, but the thermal calibration of the galvanometer may be checked with ease as often as desired. There can be no doubt that for practical purposes this apparatus is exceedingly convenient. Nevertheless the measurement of electromotive forces by the zero methods here discussed retains an advantage over current measurement, because measurements of electromotive force made at one time may be at once compared with corresponding measurement made at any subsequent time. The data are easily expressed in terms of a fixed absolute standard, in other words. All this is much more difficult in the case of current measurement, even if it were as accurate, for current measurement brings in the arbitrary constants of the galvanometer.

EXPERIMENTAL RESULTS.

Exploration for constancy of temperature; water, aniline.—When the boiling tubes, Figs. 7 to 11, are to be used for temperature measurement, the chief point of interest is the degree of constancy attained throughout the length of the central tube into which the thermo-element is to be inserted. To obtain the requisite data it is sufficient to insert a thermo-element, the constants of which are approximately known, into the tube mentioned, with the junction consecutively at different heights above the surface of ebullition. In the following tables, therefore, the absolute values of the high temperature T is of less importance and of smaller accuracy, while the *variations* of T are represented with nicety. In the table the temperature t of the cold junction is constant; e (microvolts) is the measured electromotive force of a new element, Pt hard-Pt Ir 20 per cent., from which the temperature T is computed.

TABLE 12.—*Constancy of temperature along the axis of boiling tube. Steam.* $T=100°$.

Height of junction above bottom.	t.	e.	T.	Remarks.
Cm.	° *C.*	*Microvolts.*	° *C.*	
5	20.0	660.7	98.9	Surrounded by liquid.
10	20.0	673.0	100.1	Surrounded by vapor.
15	20.0	672.2	100.0	Do.
20	20.0	672.0	100.0	Do.
25	20.0	672.0	100.0	Do.
30	20.0	672.0	100.0	Do.
34	20.0	666.0	99.4	Surrounded by cork.
5	20.0	683.7	101.2	Surrounded by liquid; burner lowered.

This table is cited as an example of many similar observations made with like results. The adjustment of heat was nearly perfect, so that no steam escaped. The ebullition was quiet and the water was left in the tube in almost undiminished amount at the close of the experiment. The first observation 5^{cm} above bottom of tube is taken at about the middle of the boiling liquid and the temperature here depends upon whether the ring burner encircles the tube above or below this point. The next observation, 10^{cm} from the bottom, is about 2^{cm} above the surface of ebullition, and from here to the upper cork the temperature is absolutely constant. To make these explorations it is necessary that the thermo-couple be new or *perfectly homogeneous* and annealed; otherwise the error of homogeneity will be falsely attributed to an error of the constancy of the boiling tube. Exploration with a mercury thermometer is less satisfactory than the thermo-couple test because the stem of the thermometer usually projects.

Similarly constant results may be obtained with aniline at 187°, which it is therefore not necessary to cite. They show that with the junction about 1^{cm} above the zone of ebullition, quiet boiling presupposed, its temperature may be regarded identical with that of a mercury thermometer placed contiguously with the mentioned junction and inserted from above.

Exploration for constancy of temperature; mercury.—In the case of mercury the zone of constant temperature is of course much less in height, and special investigations with respect to it are therefore essential. The data in the table are given on a plan identical with the foregoing. Results are also appended for mercury impure with oxide, in which case the liquid sometimes bumps violently during ebullition. The liquid surface is at 10^{cm} from the bottom nearly.

TABLE 13.—*Constancy of temperature along axis of boiling tube. Mercury.* $T = 358^\circ$.

Height of junction above bottom.	*t.*	*e.*	*T.*	Remarks.
Cm.	°*C.*	*Micro-volts.*	°*C.*	
In liquid 5	21.5	3320	347.4	Fresh mercury; brisk and regular boiling. Liquid surface at 10^{cm}.
In liquid 10	21.5	3414	358.0	
In vapor 11	21.5	3431	357.0	
In vapor 12	21.5	3421	356.2	
In vapor 13	21.5	3410	355.2	
In vapor 15	21.5	3330	348.2	
In liquid 5	21.5	3393	353.9	Fresh mercury; brisk and regular boiling. Liquid surface at 10^{cm}. Disks in the mercury tube.
In liquid 8	21.5	3448	358.4	
In liquid 9	21.5	3436	357.4	
In vapor 10	21.5	3436	357.4	
In vapor 15	21.5	3192	356.4	
5	24.0	3425	358.2	Violent boiling with bumping. Liquid surface at 10^{cm}.
15	24.0	3393	325.3	
0	20.3	3856	391.3	Gentle ebullition with bumping. Liquid surface at 10^{cm}.
5	21.7	3300	345.8	
9	23.6	3436	358.8	
10	22.9	3431	357.8	
12	23.4	3295	346.6	
15	23.4	3090	320.1	
20	21.8	745	94.5	
25	21.8	443	58.2	
30	21.8	317	42.6	

These tables show conclusively that for a distance along the central tube of about 1.5^{cm} above and below the surface of ebullition, the temperature is that of the boiling point of mercury, with an error of less than a few tenths of a degree. The temperature of the liquid below the surface and of the vapor above it depends on the position of the ring burner and of the intensity of ebullition. The suddenness with which temperature decreases between 5^{cm} and 10^{cm} above the surface of ebullition is well shown by the data of the last part of Table 13. Hence it is permissible to speak of a zone of ebullition comprising in vertical extent about 5^{cm} of the boiling tube above the surface. The use of loose disks or screens of asbestos in the boiling space, to guide the vapor or prevent convection here, is of no obvious avail, probably from the great weight of mercury vapor as compared with that of air. These disks complicate the apparatus, and are therefore to be discarded. Table 13 is an example of many similar results. The two or three centimeters of available space for constant temperature are amply sufficient for the calibration and for many other purposes. At any given point of the space the constancy of temperature is almost perfect. If the outside of the tube is well jacketed with asbestos wicking, the height of the space of constant temperature may be much increased. It has been stated that in the data of Table 13 the variations of boiling point, and not the absolute value of the boiling point, is the point of consideration.

Exploration for constancy of temperature; sulphur.—From the nature of the case, the calibration with sulphur is more difficult, and calls for a more careful examination. Hence series of data are drawn up in Table 14, both for gentle and for violent ebullition. The condition of constancy of the center of the zone of constant temperature is also tested by a special thermo-couple, inserted from time to time during the progress of the measurements. In the first part of Table 14 the surface of ebullition is at 12^{cm} above the bottom; in the remaining parts about 8.5^{cm} from the bottom. No carbonic-acid or other gas is introduced into the tube, and ebullition probaby takes place in SO_2 gas, formed from S vapor and the oxygen of the tube. To produce very violent ebullition the copper gauze surrounding the sulphur tube was heated even to redness. As before, the variation of *T*, and not the absolute value of the boiling point, is the chief consideration.

TABLE 14.—*Constancy of temperature along axis of boiling tube. Sulphur.* $T=449°$.

Height above bottom of tube.		*t.*	*e.*	*T.*	Time.	Remarks.
Cm.		°*C.*	*Micro-volts.*	°*C.*		
In vapor.	15	15	3056	339		Burner at 10^{cm}. Liquid surface at 12^{cm}.
	14	15	4038	433		
	13	15	4203	448		
In liquid.	11	16	4226	451		
	10	16	4273	455		
	9	16	4157	445		
	8	16	3394	373		
					h. m.	
	12	16.6	4206	449.5	11 30	
	12	17.2	4198	449.2	12 10	
In vapor.	13	19.0	3923	398.9	2 15 p. m.	Mild ebullition. Liquid surface at 8.5^{cm}.
	11	19.0	4498	445.0		
	10	19.0	4517	446.5		
	9	19.0	4545	448.5		
In liquid.	8	19.0	4629	455.3		
	7	19.0	4651	456.8		
	6	19.0	4577	451.4		
	5	19.0	4078	411.9		
	4	19.0	3448	359.3		
	3	19.0	2779	301.0		
In vapor.	13	19.0	3886	395.9	3 15	Mild ebullition. Liquid at 8.5^{cm}.
	11	19.0	4487	444.0		
	10	19.0	4506	445.4		
	9	19.0	4545	448.6		
In liquid.	8	19.0	4587	452.1		
	7	19.0	4643	456.5		
	6	19.0	4509	445.8		
	5	19.0	3988	403.8		
	4	19.0	3221	339.6		

Table 14.—*Constancy of temperature along axis of boiling tube, etc.*—Continued.

Height above bottom of tube.		*t.*	*e.*	*T.*	Time.	Remarks.
Cm.		° *C.*	*Micro-volts.*	° *C.*		
In vapor.	13	19.0	4487	444.0	3 45	Violent ebullition. Liquid at 8.5cm.
	11	19.0	4496	444.7	....	
	10	19.0	4511	445.9	....	
	9	19.0	4529	447.4	....	
In liquid.	8	19.0	4597	452.7	....	
	7	19.0	4657	457.4	....	
	6	19.0	4669	458.4	....	
	5	19.0	4423	439.1	....	
In vapor.	13	19.0	4492	444.4	5 15	Violent ebullition. Liquid at 8.5cm.
	11	19.0	4502	445.2	....	
	10	19.0	4513	446.1	....	
	9	19.0	4550	448.9	....	
In liquid.	8	19.0	4609	453.6	....	
	7	19.0	4669	458.6	....	
	6	19.0	4669	458.4	....	
	5	19.0	4478	443.4	....	
	4	19.0	3900	396.9	5 30	
		16.6	4206	449.6	♃, 11 30 a. m.	Check observations made with a special thermo-couple during the progress of the above measurements. Hot junction just above surface of ebullition.
		17.2	4198	440.3	12 10 p. m.	
		19.3	4190	449.8	2 30 p. m.	
		19.2	4180	449.0	3 00 p. m.	
		20.3	4185	449.8	5 30 p. m.	
		19.8	4183	449.8	7 30 p. m.	
		14.8	4203	448.2	♀, 9 00 a. m.	
		19.4	4171	448.5	12 00 p. m.	
		18.4	4183	448.8	2 15 p. m.	
		18.7	4187	449.3	5 30 p. m.	

By *plane of ebullition*, an expression frequently to be used, I refer merely to the mean surface of the agitated liquid. Above this there is a similar well defined plane of condensation, and the zone of constant temperature lies between these planes, nearer the lower.

The data taken as a whole show that for 1^{cm} or 2^{cm} above the plane of ebullition the variation of temperature is not more than two or three degrees from the boiling point. These changes are produced by relatively great differences in the intensity of ebullition. The use of thick asbestos jackets increases the height of the space of constant temperature. As was the case with mercury, the zone of ebullition is sharply marked both above and below the surface of the liquid, and its height depends very materially on the violence of the boiling. The tube during ebullition is apt to be very dark brown, so that it is sometimes difficult to discern the boiling surface at all. It is well, therefore, to mark its position beforehand. Taking the above results as a whole, it appears that just above the surface of ebullition the temperature is constant for an indefinite period of time, and that it does not differ from the boiling point of sulphur more than a degree at most.

Exploration for constancy of temperature; zinc.—In Table 15 I give similar observations relative to the constancy of temperature along the axis of a zinc crucible. The form with open tube, Fig. 15, is used, so that the variation of temperature along as much as 14^{cm} of the axis can be measured. During measurement the central tube is closed above with a loose plug of asbestos wicking. Experiments are made with two furnaces, placed side by side and heated simultaneously. It is difficult to define the surface of ebullition with reference to the crucible, for the zinc is apt to be porous and of great bulk, and it is sure to be spattered against the top of the crucible and to solidify there. *T* in Table 15 is approximate, since the variation of *T* is alone of interest here. It was necessary to finish the observations for the first crucible before commencing those of the second.

TABLE 15.—*Constancy of temperature along the axis of the zinc crucible.* Form, cf. Fig. 15

FURNACE No. 1.

Height above bottom of crucible.	t.	e_{20}.	T.	Time.	Remarks.
Cm.	° *C.*	*Microvolts.*	° *C.*	*Hours.*	
4	21.6	11060	....	3.18	Liquid surface about 8^{cm} above bottom.
8	21.6	11060	....	3.25	
10	21.6	10950	....	3.30	
12	21.6	10670	....	3.33	
8	21.6	11090	....	3.38	
4	21.6	11090	....	3.43	
FURNACE No. 2.					
4	21.6	11040	....	3.55	Liquid surface about 8^{cm} above bottom.
8	21.6	11060	....	3.58	
10	21.6	11040	....	3.67	
12	21.6	10970	....	3.70	
14	21.6	10830	....	3.77	
10	21.9	11090	....	3.85	
8	21.9	11080	....	3.92	
4	21.9	11080	....	4.00	

To obtain a full understanding of the purport of these data it is necessary to turn to Fig. 15, p. 94, where the positions of the present points of observation have been marked with little circles. The data, therefore, show most remarkable and unexpected constancy, particularly so when compared with the results for mercury and sulphur. This is due to the fact that the distilled zinc condenses on the sides of the upper and colder parts of the crucible and then runs down on the walls—a fact well demonstrated by breakage of the crucible after the experiment. Hence the interior is practically encased in an envelope of boiling zinc, although the exterior of the crucible by actual measurement shows 1,400° and more. A significant result of these explorations is this, that the passage from the region of boiling liquid into the region of vaporized zinc is not discernible in the data. Temperature is practically constant until the upper cold parts of the crucible are reached.

PRACTICAL CALIBRATION.

Investigation of data.—Instead of extending these experiments into higher temperatures and determining further data for the fire-clay apparatus, it will be expedient to actually calibrate a series of elements. Such experiments will show both the constancy of the divers boiling points as regards time, as well as their absolute correctness as compared with the data of Chapter I. Indeed, the degree of identity exhibited by distinct series of data obtained almost a year apart, by thoroughly different methods and under different circumstances in all other respects, will be the best available criterion of the validity of the said series of results. Hence the following table is given with considerable fullness. The boiling points taken are zinc (930°), sulphur (448°), mercury (357°), aniline (measured 187°), and water. All observations are made in time series; and for the temperatures t and T of the cold and hot junctions, the electromotive force e microvolts was observed at the time specified on the same horizontal row. The mean of these isolated observations being taken, the results are used for the calculation of the constants a and b in equation (1) above, by the method of least squares; a and b are inserted in the ninth column. The fifth contains the calculated value of e, and its difference from observed e is given in the sixth column. Finally, in the seventh and eighth columns are inserted the correction $e_{20}-e$ and the value e_{20} of electro-motive force which hold for $t=20$. In addition to these data the table contains values parenthetically inserted. These are derived from the constants for the calibration if carried only as far as the boiling point of sulphur, to the exclusion of zinc. Hence these constants, being derived similarly to the extrapolation constants of Chapter I, are at once comparable with them.

TABLE 16.—*Calibration of thermo-couples Nos.* 17, 18, 22, 35, 36.

No.	t.	T.	e observed.	e calculated.	δe.	$e_{20}-c$.	e_{20}.	a and b.	Time.
	° C.	° C.	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	*h. m.*
17	20.4	930	9101	....	....	....	9101	8.049	2 24
	20.4	930	9185	....	....	....	9185	0.002357	27½
	20.7	930	9169	....	....	....	9170	....	3 00
	20.8	930	9173	....	....	....	9175	....	7
	21.4	930	9169	....	....	....	9176	....	33
	21.4	930	9152	....	....	....	9159	....	38
	21.8	930	9173	....	....	....	9183	....	4 2
	22.0	930	9169	....	....	....	9182	....	15
	22.5	930	9211	....	....	....	9227	....	40
	22.7	930	9211	....	....	....	9228	....	45
	22.8	930	9211	....	....	....	9229	....	50
	22.8	930	9211	....	....	....	9229	....	55
	22.8	930	9211	....	....	....	9229	....	56
Mean	21.7	930	9180	9354	−174	9	9190	....	

TABLE 16.—*Calibration of thermo-couples Nos.* 17, 18, 22, 35, 36—Continued.

No.	*t.*	*T.*	*e* observed.	*e* calculated.	δe.	$e_{20}-e$.	e_{20}.	*a* and *b*.	Time.
	° *C.*	° C.	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Microvolts.*	*h. m.*
17........	20.0	448	4062	(4502)	(+2)	....	4058	(7.66)	71 13
	21.4	448	4050	....	....	....	4037	(0.00390)	12 4
	22.1	448	4049	....	....	....	4065	....	33
Mean......	21.2	448	4054	3909	(+145)	5	4059	....	
17........	20.5	357	3065	(3077)	(−10)	....	3065	....	3 1
	21.0	357	3068	....	....	....	3072	....	4 37
Mean......	20.8	357	3067	3012	+55	2	3069	....	
17........	18.5	186.5	1428	(1420)	(+14)	....	1426	....	10 14
	19.3	186.8	1433	....	....	....	1428	....	51
	18.4	186.4	1435	....	....	....	1425	....	1 45
Mean......	18.7	186.6	1435	1433	+2	−10	1425	....	
17........	18.9	99.9	649.2	(659)	(−9)	....	640.6	....	12 10
	18.8	99.9	650.6	....	....	....	641.3	....	34
Mean......	18.8	99.9	649.9	676	−26	−9.3	640.6	....	
18........	20.5	930	9122	....	....	....	9122	7.973	2 35
	20.8	930	9160	....	....	....	9162	0.002352	3 15
	21.6	930	9122	....	....	....	9131	....	43
	22.1	930	9126	....	....	....	9138	....	4 18
Mean......	21.2	930	9133	9280	−147	5	9138	....	
18........	20.0	448	3998	(4005)	(−4)	....	3994	....	11 30
	21.5	448	4004	....	....	....	4012	....	12 10
	22.2	448	4000	....	....	....	4013	....	38
Mean......	20.9	448	4001	3883	+118	3	4004	....	
18........	20.6	357	3035	(3041)	(−5)	....	3036	(7.64)	3 6
	21.0	357	3037	....	....	....	3041	(0.00367)	4 42
Mean......	20.8	357	3036	2986	+50	2	3038	....	
18........	18.4	186.5	1422	(1409)	(+10)	....	1410	....	10 10
	19.3	186.8	1415	....	....	....	1410	....	55
Mean......	18.8	186.7	1419	1420	−1	−9	1410	....	
18........	18.9	99.9	647.2	(655)	(−7)	....	638.6	....	12 13
	18.7	99.9	649.2	....	....	....	639.1	....	38
Mean......	18.8	99.9	648.2	669	−21	−9.3	638.9	....	
22........	20.6	930	9198	....	....	....	9199	....	2 40
	20.8	930	9202	....	....	....	9204	....	3 17
	21.6	930	9185	....	....	....	9194	....	48
	22.2	930	9181	....	....	....	9194	....	4 22
Mean......	21.3	930	9191	9347	−157	6	9197	....	
22........	19.8	448	4030	(4025)	(−3)	....	4025	7.993	11 27
	21.0	448	4026	....	....	....	4030	0.002409	54
	21.2	448	4026	....	....	....	4031	....	58
	21.9	448	4020	....	....	....	4031	....	12 23
	22.6	448	4019	....	....	....	4035	....	53
	22.8	448	4011	....	....	....	4029	....	1 15
Mean	21.6	448	4022	3895	+127	8.6	4031	....	

TABLE 16.—*Calibration of thermo-couples Nos.* 47, 18, 22, 55, 36.—Continued.

No.	t.	T.	e observed.	e calculated.	δ e.	θ_{20} e.	e_{20}.	a and b.	Time.
	° C.	° C.	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	*Microvolts.*	h. m.
22	20.2	357	3049	(3058)	(−7)	....	3047	(7.64)	2 40
	20.3	357	3057	....	....	....	3056	(0.00381)	....
	20.4	357	3053	....	....	....	3052	....	53
	20.8	357	3051	....	....	....	3053	....	3 25
	21.0	357	3054	....	....	....	3057	....	4 30
	21.1	357	3054	....	....	....	3059	....	55
	21.2	357	3048	....	....	....	3053	....	5 25
	21.2	357	3048	....	....	....	3053	....	32
	21.0	357	3048	....	....	....	3052	....	6 40
	21.0	357	3050	....	....	....	3054	....	7 23
Mean	20.8	357	3051	3000	+51	2	3053	....	
22	18.4	186.5	1426	(1412)	(+11)	....	1414	....	10 3
	19.1	186.5	1423	....	....	....	1416	....	35
	19.2	186.8	1423	....	....	....	1417	....	45
	19.5	186.8	1422	....	....	....	1418	....	11 17
	18.3	186.4	1422	....	....	....	1409	....	1 37
	18.8	186.4	1421	....	....	....	1410	....	2 00
Mean	18.9	186.6	1423	1423	−0	—9	1414	....	
22	19.1	99.9	646.7	(656)	(—7)	....	639.7	....	12 5
	18.9	90.9	647.8	....	....	....	639.2	....	20
	18.8	90.9	650.6	....	....	....	641.3	....	12 26
	18.6	90.9	651.0	....	....	....	640.1	....	50
Mean	18.8	99.9	649.0	671	−22	—9.3	639.7	....	
35	20.6	930	10226	....	....	....	10226	7.776	2 48
	21.0	930	10214	....	....	....	10218	0.003951	3 25
	21.8	930	10219	....	....	....	10229	....	4 00
	22.2	930	10214	....	....	....	10227	....	28
	22.4	930	10257	....	....	....	10272	....	36
Mean	21.6	930	10226	10475	—249	8.6	10235	....	
35	20.4	448	4297	(4321)	(—25)	....	4296	(7.18)	11 43
	21.7	448	4297	....	....	....	4306	(0.006 27)	12 15
	22.3	448	4295	....	....	....	4309	....	42
Mean	21.5	448	4296	4108	+188	8	4304	....	
35	20.7	357	3220	(3216)	(+4)	....	3222	....	3 15
	21.1	357	3220	....	....	....	3225	....	4 47
Mean	20.9	357	3220	3119	+101	3	3223	....	
35	18.8	186.5	1434	(1420)	(+12)	....	1425	....	10 21
	19.3	186.8	1427	1438	....	....	1422	....	11 6
	18.5	186.4	1436	....	....	....	1424	....	1 53
Mean	18.9	186.6	1432	....	−6	—9	1423	....	
35	18.9	99.9	632.1	(643)	(—9)	....	623.5	....	12 18
	18.7	99.9	634.5	....	....	....	624.4	....	12 42
Mean	18.8	99.9	633.3	668	−35	—9.3	624.0	....	

TABLE 16.—*Calibration of thermo-couples Nos.* 17, 18, 22, 35, 36.—Continued.

No.	t.	T.	e ab-served.	e calculated.	δe.	$e_{20}-e$.	e_{20}.	a and b.	Time.
	° *C.*	° *C.*	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Micro-volts.*	*Microvolts.*	*h. m.*
36	20.7	930	10214	....	....	....	10216	7.785	2 55
	21.2	930	10205	....	....	....	10210	0.003918	3 28
	21.7	930	10193	....	....	....	10202	....	52
	22.3	930	10245	....	....	....	10259	....	4 33
Mean......	21.5	930	10212	10467	−255	8	10220	....	
36	20.8	448	4309	(4329)	(−26)	....	4311	(7.19)	11 49
	21.8	448	4308	....	....	....	4318	(0.00629)	12 19
	22.4	448	4293	....	....	....	4308	....	45
Mean......	21.7	448	4303	4108	+195	9	4312	....	
36	20.8	357	3217	(3214)	(+5)	....	3219	....	3 00
	21.1	357	3221	....	....	....	3226	....	4 50
Mean......	21.4	357	3219	3121	+98	7	3226	....	
36	19.0	186.5	1443	(1422)	(+13)	....	1435	....	10 31
	19.4	186.8	1436	....	−5	....	1431	....	11 10
	18.6	186.4	1437	....	....	....	1426	....	....
	18.8	....	1425	....	....	....	1416	....	2 10
Mean......	19.0	186.6	1435	1440	....	−9	1426	....	
36	19.1	99.9	631.2	(643)	(−10)	....	624.3	....	12 0
	18.6	99.9	636.1	....	....	....	625.2	....	12 48
Mean......	18.8	99.9	633.6	669	−35	−9.3	624.3	....	

From the constants contained in these tables I have calculated the values of e_{20} when the difference of temperature varies between $T-20=100°$, and $T-20=1,500°$, for the reason that I shall make use of these values below. In general there are three sets of values of e_{20} available; the first of these is calculated with the constants, including the zinc calibration; the second with the constants applying only as far as the sulphur calibration contained in this chapter; and the third with the constants applying as far as the mercury calibration contained in Chapter I. The last two sets having been made respectively in Washington and in New Haven will be so designated. To these couples are added results for Nos. 19 and 20, both of which are 5 per cent. Pt-Ir alloys. They will be referred to elsewhere.

TABLE 17.—*Values of e_{20} in microvolts.*

WASHINGTON AND NEW HAVEN.

T−t.	No. 17, e_{20} =			No. 18, e_{20} =			No. 22, e_{20} =		
	With zinc.	Without zinc.		With zinc.	Without zinc.		With zinc.	Without zinc.	
	Washington.	Washington.	New Haven.	Washington.	Washington.	New Haven.	Washington.	Washington.	New Haven.
100.......	838	821	815	830	815	813	833	817	814
200.......	1723	1719	1707	1708	1704	1704	1715	1711	1707
300.......	2655	2696	2677	2632	2666	2671	2644	2680	2679
400.......	3635	3751	3726	3603	3702	3751	3621	3726	3729
500.......	4661	4883	4852	4620	4811	4836	4646	4848	4857
600	5734	6094	6056	5687	5994	6034	5721	6046	6065
700.......	6855	7383	7339	6099	7250	7309	6843	7319	7350
800......	8023	8749	8700	7958	8580	8661	8013	8670	8714
900.......	9238	10194	10137	9165	9983	10091	9232	10096	10157
1000......	10500	11718	11654	10419	11460	11506	10497	11508	11678
1100......	11809	13319	13240	11719	13010	13179	11812	13177	13278
1200......	13165	14998	14921	13067	14634	14839	13176	14831	14956
1300......	14569	16755	16672	14462	16331	16576	14587	16562	16714
1400......	16020	18589	18500	15903	18102	18390	16045	19185	18548
1500......	17517	20602	20407	17391	19946	20281	17553	20252	20463

WASHINGTON.

T−t.	No. 35, e_{20} =		No. 36, e_{20} =		Nos. 19, 20, e_{20} =	
	With zinc.	Without zinc.	With zinc.	Without zinc.	With zinc.	Without zinc.
100........................	832	806	833	807	297	305
200........................	1743	1737	1745	1739	600	609
300........................	2733	2793	2734	2708	906	910
400........................	3801	3976	3801	3982	1218	1210
500........................	4950	5283	4948	5254	1533	1507
600........................	6177	6715	6154	6729	1852	1803
700........................	7482	8273	7470	8291	2177	2097
800........................	8868	9957	8825	9980	2506	2389
900........................	10331	11766	10316	11792	2840	2678
1000........................	11875	13700	11855	13732	3178	2968
1100........................	13497	15759	13470	15808	3520	3254
1200........................	15335	17944	15165	17988	3868	3539
1300........................	16978	20255	16936	20307	$a=2.944$	
1400........................	18837	22690	18789	22749	$b=0.000255$	
1500........................	20775	25252	20698	25319	$(a=3.065)$	
					$(b=-0.000093)$	

Discussion of data.—The most satisfactory method of discussing the results of Table 17 will consist in first mapping out its data graphically, and inserting upon the loci so drawn those results of Table 16 which are the immediate consequences of experiment. I will first consider a comparison of the results of Chapter I and of Chapter II for such cases in which the calibration was carried forward about as far as 400°, the

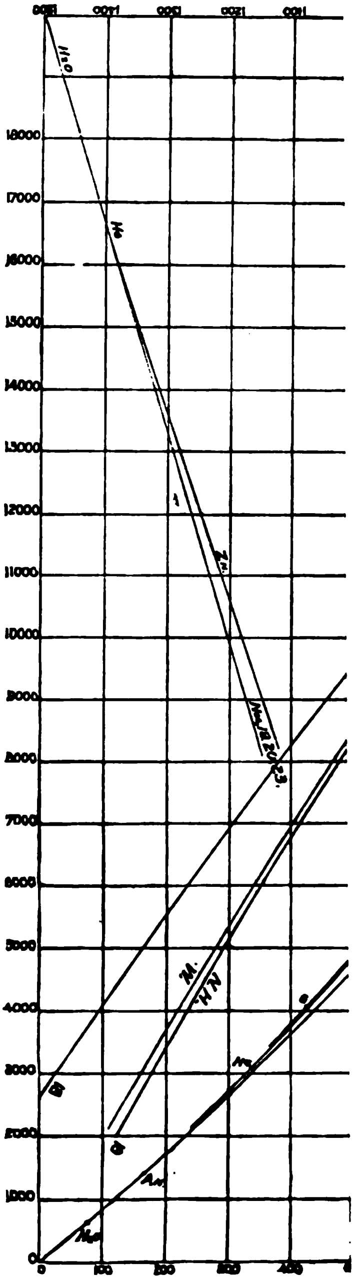

FIG. 21. Chart showing the relation of

constants then calculated from these data and used for trial extrapolations. It appears from this comparison that the results of these trials are almost perfectly coincident. In case of No. 17 the difference at 1,500° is only 4°; in case of No. 18, 14°; in case of No. 22, 9°. Now, when it is remembered that the results of Chapter I are obtained by the large vapor apparatus there described and that the results of this chapter are obtained by the small practical forms, the coincidence of the results of this exceedingly severe test is most remarkable and gratifying. In Table 16, moreover, the relatively small differences between the parenthetical results for observed and calculated *e*, is further evidence in favor of the statement just made.

If, however, we include the boiling point of zinc in the present comparisons and derive the constants by the method of least squares, the relatively large differences thus obtained at once show that the quadratic equation assumed is no longer applicable, so far as the results in hand are concerned. The loci corresponding to these new constants differ at 1,500° by amounts as follows: In case of No. 17, by 126°; in case of No. 18, by 115°; in case of No. 22, by 119°; in case of No. 35, by 126°; in case of No. 36, by 130°. Similarly the differences between observed and calculated *e* in Table 16 (without parentheses), differ by large values. To obtain a notion of the nature of this difference it is well to insert the observed result for zinc in the chart, Figs. 21 and 22. When this is done it appears that the position of the zinc point bears no observable relations to the positions of the sulphur, mercury, aniline, and water points. There are three causes for this large discrepancy to be considered: 1. Either the relation between temperature and electromotive force in case of platinum-iridium elements is circumflexed or anomalous between 500° and 1,000°; or the accepted value of the boiling point of zinc, 930°, is too large by about 75°; or the boiling point of zinc in the crucible calibration has not been reached. The last of these suppositions is easily disproved, both by the fact that during ebullition zinc dust escapes from the top of the crucible, and that after breaking the cold crucible the evidences of ebullition are apparent in drops of zinc scattered against the walls and solidified there after cooling. Again, the temperature on the outside of the crucible must have been at least 500° above the boiling point of zinc. Finally there is an almost complete coincidence between the zinc data for the large crucibles, in Chapter I, and the present data for small crucibles, as will presently be shown more at length. Hence the source of the zinc discrepancy in question is to be referred to one of two causes: either the platinum-iridium thermo-couple shows a circumflex-like anomaly in the relation between electromotive force and temperature between 500° and 1,000°, or the values heretofore assumed for the boiling point of zinc (*ca.* 930°) are too high b 75°. To decide between these two difficulties, the importance of which is here regarded merely from the standpoint of the present investigation, is not the purpose of the present chapter and will be touched upon later.

Time variations of thermo-electric data.—In this place a consideration of the degree of coincidence between present and former zinc data is pertinent. In the results given in Table 6, Chaper I (p. 78, June 11). the values for the boiling point of zinc if expressed in (reduced) units of elctromotive force were:

Microvolts.
No. 17............ $e_{20}=9220$
No. 18............ $e_{20}=9180$ (188)
No. 22............ $e_{20}=9240$

These values are available for comparison with the data of Table 16, Chapter II, from which the corresponding mean values are found to be:

Microvolts.
No. 17............ $e_{20}=9190$
No. 18............ $e_{70}=9140$ (188)
No. 22............ $e_{20}=9200$

This slight difference of less than ½ per cent. in the values of e_{20}, and which amounts to only about 3° of temperature, is quite negligible and easily referable to the incidental errors of experiment. In the large furnaces of Chapter I such an error is possible, even at the cold junction.

Duration of continued ebullition, constant high temperatures.—This brings me finally to a consideration of the constancy of the boiling point as observed with the crucibles described, when this constancy is considered with reference to the time during which ebullition has been going on. A series of such results are given in Table 16, and if necessary others may be supplied during the course of the discussion. Turning first to the results, e_{20}, for zinc, it appears that after the value of T has become constant at about 3 o'clock, the variation in e_{20} from this time until 5 o'clock (9180 microvolts to 9230 microvolts) are only a little more than ½ per cent. of e_{20}, corresponding to about 4° centigrade for the two hours of ebullition. This variation is an almost regular increase of T. This strikingly perfect degree of constancy of the temperature of this crucible is additionally attested by the values of e_{20} for the elements Nos. 18, 22, 35, 36, to which I might add many other results, were it at all necessary to supply further corroboration. By way of illustration, merely, I will give a few data obtained when the contents of the crucibles are antimony or bismuth instead of zinc. I will also add some results derived from commercial cadmium. In the case of bismuth the walls of the cold crucible, after boiling, were lined above the surface of the metal with a fine granular coating of bismuth, and very near the surface a narrow zone of little bismuth beads was apparent. Nevertheless, ebullition can only have commenced, as is proved by the thermo-electric data, and the incrustation is due to volatilization

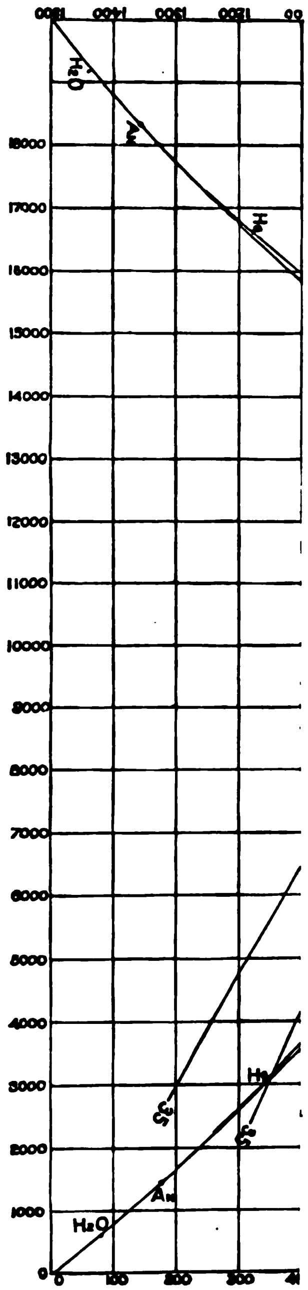

FIG. 22. Chart showing the re

below the boiling point. The temperature in the cases of both bismuth and antimony was sufficiently high to partially fuse the porcelain insulator, and to cause it to stick fast in the central tube. This is a great annoyance, because platinum at high white heats has only small tensile strength, and is therefore easily pulled apart in the endeavor to withdraw the element from the tube. The difficulty is obviated by using fire-clay insulators.

TABLE 18.—*Crucible, Fig.* 13, *charged with bismuth.*

No.	t.	e.	e_{20}.	Time.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h. m.*
17	19	8300	8300	2 00
	19	10710	10700	5
	19	11340	11330	6
	19	12010	12000	7
	19	12780	12770	10
	19	13670	13660	15
	19	14150	14140	20

The crucible after the last measurement, being fluxed through, began to leak, putting an end to the experiment. The value of T would of course only be approximate if obtained by using the zinc constants of Table 16 for extrapolation. Nevertheless; the continued rapid increase of temperature, T, shows that the boiling point has as yet by no means been reached. The behavior is therefore in striking contrast to the zinc-charged crucible.

TABLE 19.—*Crucible, Fig.* 13, *charged with antimony.*

No.	t.	e.	e_{20}.	Time.
	° *C.*	*Micro-volts*	*Micro-volts.*	*h. m.*
17	20	12410	12410	6 42
17	20	12730	12730	45
17	20	12790	12790	46
17	20	12900	12900	48
Element No. 17 pulled apart on withdrawing it, No. 18 substituted for it.				
18	22	12810	12830	7 25
18	23	13210	13230	30
18	23	13210	13230	32
18	23	13390	13410	36
18	23	13520	13540	40
18	24	13600	13640	42

Here the remarks already made under bismuth nearly apply. The crucible leaked after the last observation, and the experiment had therefore to be discontinued. T would have the approximate signification stated. The porcelain tubes again soften.

In operating upon cadmium, I first tried glass tubes. But after many trials the experiment was abandoned, both because of the decidedly reduced viscosity of glass at low red heat, and because the simple ring burner, even while a powerful pair of bellows is used to intensify the blast, is not capable of easily boiling cadmium. Hence the clay crucibles were used and results were obtained as follows. The value of T is here appended, as derived from Table 16, both for the case in which the exterpolation is made with zinc, and as made without zinc. The cadmium used is of commercial purity only. What I aim at here is a mere illustration of method.

TABLE 20.—*Crucible, Fig.* 13, *charged with cadmium.*

No.	t.	e.	e_w.	Time.	Cum zinc T.	Sine zinc T.
	° C.	Microvolts.	Microvolts.	h. m.	° C.	° C.
17	21.2	7568	7577	12 38	783	734
17	22.8	7626	7648	1 0	790	740
17	23.8	7558	7588	18	783	735
18	21.6	7541	7553	12 43	785	743
18	22.9	7528	7550	1 3	785	743
22	21.9	7568	7583	12 47	784	740
22	23.1	7577	7601	1 6	785	742
35	22.2	8346	8363	12 52	785	725
35	23.2	8337	8362	1 10	785	725
36	22.5	8333	8352	12 55	784	724
36	23.5	8325	8352	1 12	784	724

The results are given here chiefly by way of contrast with the above tables for bismuth and antimony, since they show an admirable degree of constant temperature maintained for nearly one hour at a relatively low temperature. Inasmuch as the interval between 500° and 1,000°, if the assumed boiling point of zinc be correct, is anomalous and not simply quadratic, the interpolation here made for the measurement of T is unsafe. Hence I have given T both as exterpolated from calibrations (0° to 450°) excluding zinc, and as interpolated from calibrations including zinc. If there were no anomaly the constancy of the values of T found by operating with divers elements would make these results very trustworthy.

I have made other similar experiments with selenium and with zinc chloride; but respecting all of these the remarks made for cadmium apply. Further data are therefore omitted here.

Duration of continuous ebullition, low temperatures.—Returning from this digression, I will next exhibit the constancy of temperature for the time series of boiling-point experiments made in the glass boiling tubes. The data of Table 16 are again available with a few supplementary results to be inserted below. The variation of temperature during about an hour's uninterrupted boiling in sulphur in case of No. 17 is within $\frac{1}{3}$ per cent. of e_{20}; in case of No. 18 about $\frac{1}{2}$ per cent. of e_{20}; in case of No. 22 within $\frac{1}{3}$ per cent. of e_{20} for almost two hours of boiling, etc. The constancy is satisfactory, and since the variations contain incidental errors it is probable that the boiling point itself is reached to within two or three degrees. To test this supposition I reversed the procedure, and by means of the given constants measured the boiling point of sulphur with the following results:

TABLE 21.—*Constancy of temperature in boiling tubes. Sulphur.*

No.	t.	e.	e_{20}.	T.	Time.
	° *C.*	*Micro-volts.*	*Micro-volts.*	° *C.*	*h. m.*
17	20.4	4005	4008	445	11 15
	20.4	4005	4008	445	23
18	20.9	3974	3981	445	11 25
	21.2	3967	3976	445	32
22	21.5	4000	4012	446	11 37
	21.7	4000	4013	446	40

These results corroborate the statements made. All these data are obtained with older forms of apparatus. I believe that if I were to repeat them with the newer forms (Figs. 14, 15) the limits of error would be much decreased and the experiment materially gain in certainty.

Remarks of the same nature as the above apply to mercury, for which the conditions of constant temperature are much more favorable. A long time series was made with element No. 22, where ebullition was purposely prolonged nearly five hours. The total variation of boiling point is here about $\frac{1}{3}$ per cent. of e_{20}. This variation, too, is incidental, and is largely due to the fact that here, as in the case of sulphur, a gentle current of carbonic acid circulated through the tube. In later experiments I observed an almost absolute constancy; but it is not necessary to multiply these data here.

What has been said of sulphur and mercury is, of course, eminently true of lower boiling points, like aniline and water, as Table 16 aptly shows. In case of substances which boil at lower temperatures still, like alcohol and ether, special devices for condensing the vapor in the lateral tube, which projects above the boiling tube, Fig. 9, must be resorted to.

Available substances of fixed boiling points.—With these results in hand I thought it advisable to test the availability of a few organic and other substances of fixed boiling points. Usually such substances, even liquids like aniline, char or become so heavily gummed during ebullition as to vary the boiling point very perceptibly. Results of of this kind are succinctly given in the following table. Succinic and pyrogallic acid, for instance, are failures, whereas naphthaline, benzoic acid, and camphor, when heat is applied gently and gradually, supply almost as fixed a boiling point as inorganic substances. In the case of solids like the present there are two distinct planes of demarkation observable. The first of these is the plane of ebullition, and coincides with the mean surface of the agitated liquid. The other is the plane of condensation or of solidification, and is marked by an opaque ring of the substance encircling the inside of the tube. The distance between these planes can be enlarged at pleasure by cautiously increasing the intensity of the flame of the ring burner, or by surrounding the boiling tube with a thick jacket of asbestos wicking. Of course it is advisable to insert the hot junction in vapor just above the plane of ebullition. Most of the results of Table 22 are obtained by older and more primitive forms of apparatus, and could be much improved by conducting the experiments in the new forms. The table also contains corrosive sublimate, which has a very convenient boiling point for many purposes.

TABLE 22.—*Available substances for boiling-point experiments.*

Elem. No.	Substance.	e_{30}.	*T.*	Time.	Remarks.
		Micro-volts.	° *C.*		
36	Corrosive sublimate, $HgCl_2$.	2632	300	Not taken.	Apparatus closed by corks, both of which are charred.
		2627	300		
		2606	290		
		2639	301		
		2649	303		
		2631	300		12cm above surface of liquid (melted $HgCl_2$). In vapor.
		2631	300		6cm above surface of liquid. In vapor.
		2647	303		0cm above surface of liquid.
36	Succinic acid ...	2094	255	Not taken.	The acid boils brown, *i. e.*, chars and gums ∴ boiling point rises rapidly.
		2088	255		
		2104	256		
		2240	270		Ebullition intensified.
		2300	276		Liquid very dark brown.
				h. m.	
36	Naphthaline....	1741	210	1 45	Boils well and clear; combustion tube element 2cm above surface of liquid. Very distinct planes of demarkation.
		1696	205	55	
		1696	205	2 0	
		1691	205	8	
		1679	204	15	
		1692	205	20	
		1730	209	55	More naphthaline added. This obviously changes the composition of the mass and the boiling point.
		1730	209	57	
36	Pyrogallic acid..	1818	218	....	No constancy of temperature. Decomposed, forming a viscous mass.

TABLE 22.—*Available substances for boiling point experiments*—Continued.

Elem. No.	Substance.	e_{20}.	*T.*	Time.	Remarks.
		Micro-volts.	° *C.*		
36	Benzoic acid....	1781	209	2 25	Boils quietly; perhaps more so than naphthaline.
		2071	254	30	
		2071	251	37	
		2071	254	45	
		2071	254	3 0	
		2077	255	25	
		2077	255	35	
36	Camphor	1632	209	4 0	Boils quietly. Preferable to benzoic acid. Scarcely changes color. Inodorous.
		1638	210	15	
		1638	210	20	
		1645	211	45	
		1649	211	5 15	
		1642	211	35	
		1640	211	6 0	Distance between planes of demarkation = 12cm. Asbestos jacket even red hot at one point.
		1634	210	6 0	— > just below upper plane of demarkation.
		1644	211	6 0	— > just above lower plane of demarkation.

Data for the variation of boiling point with pressure with a special view to thermometric application have been investigated for naphthaline (218°) and benzophenol (306°) by Crafts.[1] The possibility of using selenium in glass boiling tubes has been demonstrated by Troost.[2] V. Meyer[3] has made use of amylbenzoate, diphenylamin, and phosphorous pentasulphide.

Volatilizing points.—In addition to the experiments on boiling points, I made an attempt to utilize the above apparatus for measuring points of volatilization. Professor F. W. Clarke suggested the arsenic point as a desirable and insufficiently known datum and Mr. G. F. Becker made a special request for the point of volatilization of cinnabar. With both of these substances as well as with sal ammoniac I made large numbers of experiments, but failed in getting satisfactorily constant and reliable results. The effect of applying the ring burner around the sublimable solid in the tube is to form a very perfect hyperboloid of one nap, as it were; a figure, in other words, which resembles in form a united stalactite and stalagmite. The effect of heating is to volatilize the solid around the plane of the ring burner, and condensation takes place above and below the plane, forming the figure specified. A priori, it might be argued that so long as the hyperboloid remains intact and completely envelops the thermo-element, so long will the temperature of the junction not increase above the point of sublimation of the substance. Except in

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[1] Crafts, Chem. Ber., vol. 20, 1887. p. 709.

[2] Troost, C. R., vol. 95, 1882, p. 30.

[3] Goldschmidt u. Meyer; Chem. Ber., 1882, vol. 15, p. 137.

the case of H_4NCl, in which sublimation is very rapid, I was not able by using the tubes to obtain very distinct points of sublimation, showing an unmistakable tendency of these substances to superheat, or at least to contain superheated vapor in the interstices of the mass. Arsenic, for instance, forms a distinct mirror on the tube before any constancy of temperature is reached, and, moreover, the temperature may be increased above this point almost to the limits of heating capacity of the burner. In the case of cinnabar the conditions are still further complicated by the tendency of this substance to decompose in air at high temperatures. It is necessary, therefore, to pass through the tube a current of carbonic acid. By doing so, however, the tendency to irregularities of thermal constancy are much increased. For the reasons stated I think it preferable to withhold my data from this chapter altogether, and to publish them in connection with certain experiments on the relation between boiling point and pressure which I have in view. For such experiments the above apparatus, Fig. 11, is eminently fit. Possibly if the given substances be under sufficient pressure to liquefy them at the subliming point, a true value for the temperature of ebullition may be found.

Subsidiary data.—In conclusion I desire to insert here a number of subsequent results, the electro-motive force of which is given on a different scale from that heretofore adopted. These data are not to be put in relation with the results given above, but are subsidiary as regards the matter discussed in Chapter IV, on which they have an important bearing. In each case the apparatus used to obtain them has been the perfected form, and the results are therefore as trustworthy as my methods can make them. Allowing for the difference in the assumed value of the standards used, they agree with such results as have already been given, with all desirable nicety.

TABLE 23.—*Calibration in zinc vapor, December* 10, 1886.

[Charge of crucible, 9 ounces.]

No.	t.	e.	e_{20}.	Time.		Mean e_{20}, 37, 38, 39, 40.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h.*	*m.*	*Microvolts.*
22	20	9830	9830	2	15	11033
35	21	11070	11078		20	
36	22	10980	10997		25	
37	23	11010	11036		30	
22	24	9780	9814		35	
38	25	10980	11023		37	
39	26	10980	11031		40	
40	27	10980	11040		45	
22	28	9735	9803		55	
22	28	9780	9848	3	00	

The following results were obtained at a later date. The thermocouples are tested in three different furnaces, placed side by side and heated at the same time to different degrees of redness. The mean temperature of the outside of crucible was measured and found to be 1,400°.

TABLE 24.—*Calibration in zinc vapor, November* 10, 1887.

Couple No.	t.	e.	e_{20}.	Time.	Furnace No.	Mean e_{20}. 37, 38, 39, 40.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h. m.*		*Microvolts.*
37	20.8	11065	11070	1 40	1	11074
37	21.2	11065	11070	1 50	2	
37	22.8	11050	11070	2 5	3	
38	23.6	10995	11030	2 14	1	
38	24.0	11013	11050	2 20	2	
38	24.8	11030	11070	2 30	3	
39	25.3	11040	11080	2 40	1	
39	26.0	11075	11130	2 45	2	
39	26.6	11030	11090	2 50	3	
40	27.0	10995	11050	2 55	3	
22	27.3	9883	9950	3 0	3	

TABLE 25.—*Calibration in tin.*

No.	t.	e.	e_{20}.	Time.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h. m.*
22	20	15630	15630	6 30
35	21	18460	18468	35
22	21	15860	15868	40
22	22	15300	15317	40
22	23	16100	16126	40
36	24	18950	18984	50
37	25	18950	18993	55

An accident here stopped the experiment at intense white heat. It has been stated that a thick, viscous slag soon forms over the surface of the tin and the walls of the crucible, wholly enveloping the metal within it. A criterion for the boiling point of tin, therefore, will continue to be difficult of determination.

TABLE 26.—*Calibration in bismuth.*

No.	t.	e.	e_{20}.	Time.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h. m.*
22	20	11790	11790	6 0
22	20	12620	12620	5
22	20	13940	13940	15
22	20	14800	14800	25
22	20	15780	15780	30
22	20	16380	16380	35
22	20	16510	16510	40
22	20	16630	16630	45
22	20	15550	15550	50
22	20	16900	16900	55

This is very nearly the electric datum for the boiling point of bismuth, at least globules of bismuth are scattered around the walls of the crucible. The bismuth slag is not so dark and opaque as the antimony slag, indeed, often quite colorless.

TABLE 27.—*Calibration in antimony.*

No.	t.	e.	e_m.	Time.
	° *C.*	*Micro-volts.*	*Micro-volts.*	*h. m.*
22	20	15200	15200	6 10
	20	16000	16000	15
	20	17550	17550	20
	20	18000	18000	25

In these experiments intense white heats are produced by firing the furnace with two parallel blast burners, opposite in direction so as to blow a vortex of flame in the furnace. The crucible is finally corroded through, the antimony forming a corrosive opaque glaze with the clay of the crucible. A few small globules up as high as the *flat* lid of the crucible (Fig. 14) indicated very approximate ebullition.

Many other experiments of the same class were made, in all of which the intensest degrees of white heat obtainable in the furnace (Fig. 14) were applied. Two and even three injectors were inserted, the blasts for which were furnished by a large bellows of Fletcher's pattern, run by a one horse power gas-engine. The data are subservient to the investigation in Chapter IV, where the attempt is made to calibrate the thermo-couple by direct comparison with the gas-thermometer. In this place, however, it is well to remark that definite data on the boiling point of antimony, bismuth, lead, tin, etc., will probably not be attainable by such a method as the present, except by heating these substances intensely in vacuo. Such experiments I hope to make at an early date, using for this purpose the form of crucible, Fig. 14*a*, which can be hermetically sealed. (See Preface, page 22.)

FIG. 23. Apparatus for melting-point of platinum.

Thermo-electric datum for the melting point of platinum.—Finally, it is interesting to contrast these high-temperature data with the values obtained when the junction of the platinum-platinum-iridium thermo-couple is heated by the oxyhydrogen blow-pipe to extreme degrees of fusion. It is necessary for this purpose to make a thermo couple of very thick wires and to insulate them by aid of tubes of calcined lime. In Fig. 23 a convenient method of experiment is shown. *A A* is a block of lime into which two capillary holes have been drilled, just large enough to receive the wires β and γ of the thermo-couple. These are united above by a little button of platinum lying at the base of a spherical cavity in the block *A A*. *B* is an oxy-hydrogen blow-pipe by which the button is fused. A lid of calcined lime similar to the block *A A* in form but having a lateral outlet opposite *B* may be added. But the ignition is intense enough without this.

In the following table are given the values for e_{20} obtained by heating the button in the open hearth, Fig. 23. The thermo-couple is old No. 18, the wires of which have been fused and drawn over again.

TABLE 28.—*Thermo-electric datum for temperatures above the melting point of platinum.*

No.	*t.*	e_{20}.	Time.	Remarks.
	° *C.*	*Micro-volts.*	*h. m.*	
18	20	20400	1 48	First experiment.
	20	20000	2 50	Second experiment. Fresh block of lime.
	20	20100	3 00	
	20	20000	5 33	Third experiment. Fresh block of lime.
	20	20400	50	

The curiously constant electrical result for the temperature of the oxyhydrogen flame under the given circumstances is remarkable. It is interesting to note that when by any accident metallic connection is broken, there at once appear violent polarization disturbances. This shows that at the temperature of the OH_2 blow-pipe, lime is quite a good conductor of electricity, for it is less probable that under the given conditions conduction should take place through the hot gases.

The thermal equivalent of the value of *e* in hand, however, is only 1,600°, a datum certainly too small by 200° or more. This small value is significant.[1] It is in accordance with the small thermal datum for the boiling point of zinc, calculated from thermo-electric data, which apply only for the interval 0° to 400° (cf. p. 116). Hence it appears that the equation $e=a\tau+b\tau\sigma$ is an approximation, and that in high temperature work the term

$$c\,(T^3-t^3)$$

can not be neglected. This is equivalent to saying that, apart from considerations involving the Thomson effect, the electro-motive force at each junction of the thermo-couple has virtually the form

$$e=a\,t+b\,t^2+c\,t^3+\;\;.\;\;.\;\;.\;\;.$$

and that the real nature of the function *e* is not known. It is probable, however, that for practical thermometry an equation with three constants will suffice for all attainable ranges of temperature.

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[1] Cf. Introduction, pp. 49 and 50.

CHAPTER III.

CERTAIN PYRO-ELECTRIC QUALITIES OF THE ALLOYS OF PLATINUM.

EXPLANATION.

The immediate object of the investigations given in this chapter is to determine the approximate effect produced on the galvanic and the thermo-electric properties and on the density of platinum by alloying this metal with small amounts of some other metal. Not being sufficiently versed in the chemistry of the platinum group myself, and not wishing to burden my associates with the tedious task of rigorous chemical purification, I contented myself with a practical survey of the electrics of the platinum metals; nor was there enough time at my disposal to justify the attempt of an exhaustive examination.

The plan which under these circumstances suggested itself to me was to have a homogeneous ingot of platinum drawn down to a single length of tolerably thin wire, and then to compare the electrics of consecutive parts of this wire in their original and alloyed state with each other. A coil of wire consisting of a single length about 131 meters and weighing nearly 420 grains was drawn down for me by the Malvern platinum works. The wire itself, weighing about 3.2 grains per meter, was nearly 0.043^{cm} in diameter. I was the more easily able to acquiesce in this simple method of obtaining a platinum body for the alloys since, in earlier experiments of our own, samples of platinum and platinum alloys obtained in Paris could be fused over without producing any serious variation of constants, and since I inferred from the researches of Deville and Troost that the intense heating of platinum on a lime hearth before the oxyhydrogen blow-pipe, was itself a sufficient method of purification so far as the elimination of volatile and oxydizable constituents is concerned. Moreover, it has been stated in Chapter I that the general plan of work was to be such that special stress might be put on the effect of vanishing quantities of an alloying metal added to platinum. Hence I looked principally to obtaining a metallic body for the alloys showing fixed properties before and after melting.

In the course of the investigation, however, it became painfully obvious that the labor of making the alloys, the fusions, rolling and wire drawing, the experimental evaluation and the computation of the constants had been very much underrated. I found, in other words, after about one-half of my investigation had been completed, that the amount of work expended could have been justified only if the work had been begun with absolutely pure materials. I found, too, that the purity tests which had originally been made were not rigorously sufficient; that portions of the single wire of platinum lying far apart differed more seriously in their electrics than I had apprehended, and that the platinum itself when exposed before the oxyhydrogen blow-pipe during long intervals of time (several hours) showed very measurable changes of the constants which had originally characterized it, and must therefore have changed somewhat in composition. An exhibit of the numerical values of all discrepancies here involved will be given in the course of the chapter.

When so large a part of the investigation had been completed, however, it seemed expedient to push it to a close; for the classification diagram of the platinum alloys, which I was desirous of evolving, could not lead to serious misapprehension if only the scale of representation be chosen sufficiently small; if the profile, in other words, were reduced to a sufficiently small scale to make the errors negligible. Indeed, this appeared desirable because no general study of the electrics of the platinum alloys as complete as my own has as yet been made. Again, since in the scheme of fusing 2 per cent., 5 per cent., and 10 per cent. alloys, it was customary to use consecutive lengths of the platinum wire, the results at least show the effect of alloying a specified metal to a given body of platinum. Finally, the plan of operation by which the work was done is worthy of description, and with the amount of experience gained in prosecuting this tedious research I will, at an early opportunity, be able to repeat the work and bring the constants fully up to the standard of accuracy desired; in other words, to make the chemical measurement compatible with the electrical measurements.

Despite the discrepancies mentioned, this chapter is not barren in special results; and perhaps my main motive in publishing the data is due to the fact that they lead to a relation between the electrical conductivity of platinum alloys and the temperature coefficient of that conductivity, which is so nearly independent of the (alloyed) composition of the metals that I feel urged to ascribe to it the importance of a law. Very clearly does this appear when the present results for alloyed platinum are compared with a series of corresponding results long since found by Dr. Strouhal and myself when working with steel. I fully believe that in endeavoring to explain the mechanism of electrical resistance, the law in question will be more fruitful in suggestions than any allied phenomenon which has yet been investigated. Inasmuch as fused platinum appears to be the universal solvent for metals, the incontestable importance of series of data such as I here endeavor to investigate is more obvious in proportion as the number of metallic combinations obtainable is larger.

To recapitulate, therefore, the law in question (I use the term "law" simply to facilitate expression) is independent of the ingredients of the alloy except in so far as they modify its electrical conductivity. Alloying is here merely a method of modifying resistance, and the results are studied with regard to the resistance produced, not with regard to the way in which resistance is modified. In all of this work the chief object is to get nearer the true nature of electrical resistance, as a means possibly subsidiary to arriving at some results relative to the nature of electricity itself.

FUSION AND MECHANICAL TREATMENT OF THE ALLOYS.

Fusion, rolling.—It has just been stated that it was my purpose to obtain groups of 2 per cent., 5 per cent., and 10 per cent. platinum alloys of as many metals as possible. The quantities were therefore weighed out in proper proportion and fused on a lime hearth, before the oxyhydrogen blow-pipe. The blow-pipe is identical with the one described in the next chapter. The hearths consisted of cubes or rectangular solids, cut with a hack saw from a large lump of lime as free from fissures as possible. Into each of the sides semicircular cavities were dug, with a semicircular faced drill, on the lathe. Nickel, gold, copper, palladium, and tin were quietly absorbed by the melted platinum globule. Silver boiled perceptibly. Iron, and more particularly aluminium and manganese, were absorbed explosively. Chromium, cobalt, and even iridium were apt to splutter. Zinc, molybdenum, antimony, bismuth, lead, must be frequently added, but the quantity absorbed was usually sufficiently large to change the qualities of platinum perceptibly. With regard to rolling, it may be stated that the 10 per cent. gold and the 10 per cent. tin alloys are too brittle, and must therefore be diluted with further amounts of platinum. In the same way 5 per cent. chromium, 5 per cent. aluminium, 10 per cent. copper, and 10 per cent. nickel alloys, and others, usually break on rolling. Cobalt alloy, moreover, a sorbs gas and inflates itself on cooling. Iron alloy, 10 per cent., could be rolled by superficially fusing the rifts. This expedient, though not rigorously in favor of homogeneity of composition, had to be frequently resorted to; for instance, in case of antimony, bismuth, zinc, silver, and lead alloys which are more or less porous after fusion. Curious properties seem to be possessed by the tin alloys, inasmuch as the 10 per cent. alloy is brittle and hard enough to scratch iron. Experiments were made in rolling hot ingots, but with doubtful success, the quantities being too small to retain their heat for any length of time. I add, finally, that the work threw some light on the conditions of diffusion of any liquid metal in any other liquid metal, a phenomenon as yet imperfectly known.

Preliminary data, density.—In all about fifty-two alloys were fused to buttons. These were then rolled to little bars of platinum about $10^{\rm cm}$ or more in length, and about $0.013\ \square^{\rm cm}$ in section. Alloys of this length and section are suitable for preliminary measurements of resistance and density. The data for density are given in Table 29. They were obtained by suspending the platinum rods from a fiber of silk in a long stand-glass of distilled water and making the customary measurements. To make the process more convenient the left-hand scale-pan was replaced by a special lateral arm, being virtually a bent lever, the weight of which was concentrated as near its lower end as practicable, in order that the platinum rod might be hung as far from the center of figure or standard of the balance as possible. In this way abundant room for the stand-glass was easily secured. Measurements of density are subservient for the calculation of specific resistances, but they have an intrinsic value of their own.

Table 29 contains the results of the density experiments. In it l, q, and m refer to the length (^{cm}), the section ($\square^{cm}$), and the mass (g) of the bars of alloy. Δ_t and Δ_0 denote their densities at $t°$ and $0°$, respectively. The alloys are usually arranged in series of increasing percentages of alloy, but where more than three alloys are examined these percentages must be inferred from the values of Δ_0. Special analysis of all the wires would be superfluous, for the reasons stated in the introduction. The results are intended to be purely physical.

TABLE 29.—*Density of platinum alloys.*

No.	Alloy.	l	q	m	t	Δ_t	Δ_0	Δ_0 *Mean.*
					°			
0	Platinum	22.80	0.01233	5.9889	19.5	21.305	21.321	
0	....do	22.18	1187	5.6108	18.0	21.297	21.311	
0	....do	22.18	1187	5.6108	12.6	21.303	21.313	21.315
1	Gold	15.46	0.01333	4.3877	20.0	21.290	22.306	
1	....do	15.45	1335	4.3877	13.2	21.260	21.270	21.288
2	....do	15.50	1343	4.4177	20.2	21.206	21.222	
2	....do	15.48	1345	4.4177	13.4	21.211	21.221	21.221
3	....do	35.80	0746	5.6434	13.4	21.128	21.138	
3	....do	35.82	0743	5.6433	20.3	21.191	21.207	21.172
4	Silver	15.22	0.01285	4.1344	20.3	21.138	21.154	
4	....do	15.23	1282	4.1346	13.5	21.163	21.173	21.163
5	....do	23.98	1263	6.3454	13.6	20.991	21.002	
5	....do	24.05	1265	6.3798	20.3	20.964	20.980	20.991
6	....do	24.05	0759	3.5377	20.2	19.380	19.396	
6	....do	24.04	0758	3.5381	13.9	19.394	19.405	19.400
7	Palladium	16.66	0.01252	4.3754	13.5	20.975	20.985	
7	....do	16.65	1250	4.3754	13.8	21.016	21.027	21.006
8	....do	16.10	1316	4.3491	14.0	20.523	20.534	
8	....do	16.11	1314	4.3492	13.7	20.535	20.546	20.540
9	....do	17.60	1280	4.4809	13.9	19.892	19.903	
9	....do	17.60	1278	4.4810	14.2	19.904	19.915	19.909
10	Iridium	16.34	0.01265	4.3896	14.3	21.237	21.248	
10	....do	16.27	1265	4.3819	14.3	21.283	21.294	21.271
11	....do	16.00	1288	4.3865	14.5	21.282	21.293	
11	....do	16.01	1289	4.3866	14.6	21.252	21.264	21.279
12	....do	17.95	1280	4.8977	14.8	21.308	21.320	
12	....do	17.85	1282	4.8804	14.8	21.306	21.318	21.319
13	Copper	15.95	0.01315	4.3335	15.4	20.662	20.674	
13	....do	15.68	1317	4.2718	14.8	20.666	20.678	20.676
14	....do	14.74	1298	3.9415	15.0	20.584	20.596	
14	....do	15.02	1293	3.0990	15.3	20.592	20.604	20.600
15	....do	17.32	1303	4.2304	15.8	[illegible]	18.797	

TABLE 29.—*Density of platinum alloys*—Continued.

No.	Alloy.	l	q	m	t	Δ_t	Δ_0	Δ_0 *Mean*
15	Copper	17.31	1302	4.2396	15.2°	18.796	18.808	18.803
48	....do	13.85	1216	3.5194	16.5	20.890	20.903	
48	....do	13.86	1213	3.5192	12.7	20.922	20.932	20.917
49	....do	13.69	1233	3.3000	13.0	19.538	19.548	
49	....do	13.69	1232	3.2999	16.8	19.560	19.574	19.561
16	Nickel	16.35	0.01261	4.2666	16.0	20.686	20.699	
16	....do	16.35	1262	4.2670	15.5	20.660	20.673	20.686
17	....do	15.73	1303	4.0777	15.6	19.876	19.889	
17	....do	15.73	1304	4.0776	16.2	19.876	19.889	19.889
18	....do	15.98	1346	4.0350	16.5	18.750	18.763	
18	....do	15.99	1347	4.0353	15.7	18.727	18.740	18.751
19	Cobalt	14.49	0.01261	3.7625	16.6	20.581	20.594	
19	....do	14.50	1261	3.7626	15.8	20.572	20.585	20.905
20	....do	15.41	1239	3.7870	16.0	19.825	19.838	
20	....do	15.41	1239	3.7868	16.9	19.831	19.844	19.841
21	....do	18.96	1299	4.7607	17.2	19.322	19.335	
21	....do	18.95	1300	4.7610	16.0	19.310	19.323	19.329
40	....do	14.20	1235	3.3455	13.9	19.059	19.070	
40	....do	14.18	1233	3.3457	17.2	19.116	19.130	19.100
41	....do	13.38	1218	3.4270	17.0	21.013	21.027	
41	....do	13.40	1220	3.4269	13.6	20.946	20.957	20.992
22	Iron	14.54	0.01242	3.7304	17.2	20.640	20.653	
22	....do	14.54	1245	3.7306	16.1	20.589	20.602	20.628
23	....do	14.92	1274	3.8640	16.0	20.316	20.329	
23	....do	14.91	1275	3.8639	17.5	20.319	20.332	20.330
24	....do	13.27	1274	3.3087	17.5	19.564	19.577	
24	....do	13.26	1273	3.3090	15.8	19.588	19.601	19.589
42	....do	13.22	1211	3.1619	12.2	19.730	19.740	
42	....do	13.23	1209	3.1618	15.0	19.747	19.759	19.750
43	....do	12.71	1227	3.2563	14.8	20.872	20.884	
43	....do	12.73	1225	3.2565	15.5	20.875	20.887	20.886
50	Steel	13.24	1228	3.1750	18.0	19.515	19.529	
50	....do	13.24	1222	3.1748	14.4	19.622	19.633	19.581
51	....do	13.00	1220	3.1627	14.5	19.942	19.953	
51	....do	13.00	1220	3.1629	16.0	19.937	19.950	19.952
25	Chromium	12.14	0.01314	3.3329	16.8	20.888	20.901	
25	....do	12.14	1312	3.3331	13.6	20.910	20.921	20.911
26	....do	14.84	1268	3.8581	13.6	20.493	20.504	
26	....do	14.84	1268	3.8580	16.9	20.507	20.520	20.512
27	....do	17.38	1314	4.6039	16.8	20.154	20.167	
27	....do	17.39	1314	4.6042	13.7	20.137	20.148	20.157
44	....do	14.64	1209	3.6762	18.4	20.761	20.775	
44	....do	14.64	1210	3.6762	14.2	20.742	20.753	20.764
28	Tin	14.34	0.01270	3.8445	16.8	21.098	21.111	
28	....do	14.34	1270	3.8447	13.6	21.096	21.107	21.109
29	....do	15.65	1337	4.3782	16.8	20.921	20.934	
29	....do	15.65	1331	4.3774	13.6	21.004	21.015	20.974
30	....do	13.85	1336	3.7835	16.8	20.438	20.451	
30	....do	13.86	1335	3.7836	13.5	20.436	20.447	20.449
31	Aluminium	12.63	0.01233	3.1842	16.8	20.444	20.457	
31	....do	12.64	1231	3.1844	10.5	20.462	20.470	20.464
32	....do	11.98	1265	3.1387	16.8	20.712	20.725	

TABLE 29.—*Density of platinum alloys*—Continued.

No.	Alloy.	*l*	*q*	*m*	*t*	Δ_t	Δ_0	Δ_0 *Mean.*
32	Aluminium	12.00	1262	3.1388	° 10.7	20.715	20.724	20.724
33	Manganese	11.44	0.01296	3.0871	11.2	20.814	20.823	
33	....do	11.44	1298	3.0872	13.8	20.779	20.790	20.807
34	....do	14.35	1287	3.5870	11.4	19.412	19.421	
34	....do	14.34	1287	3.5867	14.2	19.434	19.445	19.433
35	Molybdenum	12.87	0.01320	3.6090	14.6	21.250	21.263	21.263
36	....do	14.36	1298	3.9565	15.2	21.239	21.252	
36	....do	14.36	1296	3.9585	11.8	21.260	21.270	21.261
45	....do	13.76	1223	3.5869	13.9	21.298	21.309	
45	....do	13.76	1225	3.5869	18.4	21.281	21.295	21.302
37	Lead	16.86	0.01278	4.5626	15.5	21.167	21.180	21.180
46	....do	14.58	1212	3.7537	13.0	21.230	21.240	
46	....do	14.57	1218	3.7539	17.6	21.228	21.242	21.241
38	Antimony	17.14	0.01343	4.7703	15.8	20.722	20.735	
38	....do	17.14	1340	4.7703	12.0	20.762	20.772	20.758
39	Bismuth	13.47	0.01311	3.7398	16.1	21.166	21.179	21.179
47	....do	15.02	1200	3.8495	13.4	21.337	21.347	
47	....do	15.08	1202	3.8495	17.8	21.297	21.311	21.329
52	Zinc	13.33	0.01232	3.2990	13.6	20.065	20.076	
52	....do	13.34	1228	3.2988	18.2	20.114	20.128	20.102
54	....do	12.29	1261	3.2496	19.8	20.959	20.975	
54	....do	12.28	1262	3.2496	20.0	20.959	20.975	20.975
53	Cadmium	12.22	1254	3.2667	....	....	(21.315)	

Preliminary data, electrical resistance of rods.—Having given the values of Δ_0 it is easy to measure the resistance of the bars of platinum alloy by carefully applying Matthiessen and Hockin's[1] or other similar method. The resistometer shown in Fig. 24, is so conveniently applicable that a short description may be given of it even if its principles be well known. The apparatus may be made unusually compact by using Kohlrausch's admirable form of Wheatstone's bridge. In practice it is conveniently inserted in the same circuit with the thermopile adjustment, and the two Daniells used as a source of current. All circuits are to be made momentarily, of course.

In Fig. 24 the Kohlrausch bridge is shown at *A*. *B* is the attachment for small resistances, *D* the standard with which they are to be compared. Let *s s* be the small platinum rod to be tested. It is firmly clamped down by the insulated levers *m m*, which properly insert it in the bridge circuits. *m m* and the similar levers *nn*, *nn*, may be moved along a stout horizontal rod at pleasure, and then clamped in any position. The part of *s s* to be electrically studied is stepped off by the rider *e*, the points of contact of which are knife edges at a known distance apart. The rider is also capable of being slid along a horizontal rod, parallel to the rod carrying *nn*, etc. When in use *e* is held down

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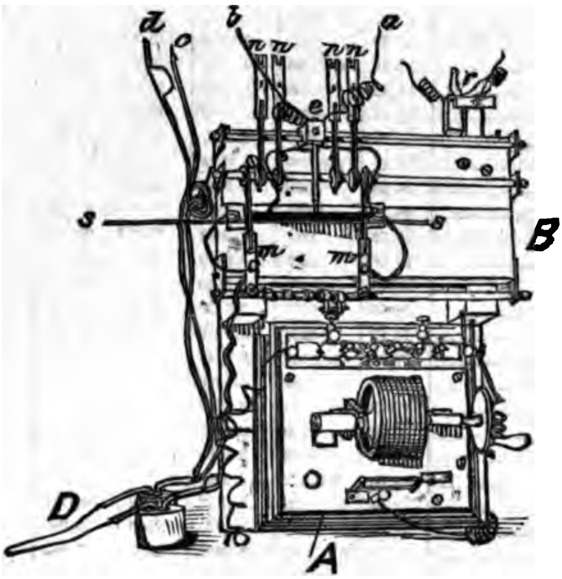
[1] Cf. Maxwell: Electricity and Magnetism, 2d ed., 1881, p. 444.

by a suitable spring. One of these riders (Fig. 25) is detached, and shown at *r*. In using Matthiessen and Hockin's method, it is merely necessary to connect *a*, *b*,....*e*, *d*, successively with the galvanometer.



Figs. 24 and 25. Resistometer with detached rider. Scale ⅓.

Table 30 contains the numerical results investigated by aid of this apparatus. r_t is the resistance (ohms) at the temperature t for the section q ^{cm}, and s_t the corresponding specific resistance (microhms). The length of rider indicates the efficient length of platinum rod for which any datum applies. The value of s_t in parenthesis refers to thin wire as containued in Table 31.

TABLE 30.—*Electrical resistance of platinum alloys (thick wires).*

[rider – length = 10.04^{cm}.]

No.	Alloy.	r_t	t	q	s_t	(s_t)
0	Platinum	1245	20	0.01233	15.35	15.55
0	....do	1285	18	0.01187	15.26	15.55
1	Gold	1424	20	0.01333	18.98	19.23
2	....do	1678	21	1343	22.44	22.73
3	....do	3441	21	0743	25.58	25.91
4	Silver	1516	22	0.01285	19.48	19.73
5	....do	1802	22	1265	22.79	23.09
6	... do	4586	22	0759	34.80	35.25
7	Palladium	1560	21	0.01252	19.53	19.79
8	....do	1628	20	1314	21.40	21.68
9	....do	1864	20	1280	23.86	24.17
10	Iridium	1571	17	0.01265	19.87	20.13
11	....do	1642	17	1289	21.17	21.44
12	... do	1909	17	1280	24.43	24.75

TABLE 30.—*Electrical resistance of platinum alloys (thick wires)*—Continued.

[rider=length−10.04^{cm}.]

No.	Alloy.	r_t	t	q	n	(n)
13	Copper	2397	16	0.01315	31.51	31.92
14	....do	2628	17	1293	33.97	34.41
15	...do	4899	17	1303	63.82	61.65
48	....do	2118	17	1216	25.69	26.18
49	....do	4531	17	1232	55.87	56.92
16	Nickel	1739	18	0.01261	21.93	22.22
17	....do	2110	18	1304	27.51	27.87
18	....do	2503	18	1346	33.71	34.14
19	Cobalt	2379	18	0.01261	30.01	30.40
20	....do	3245	19	1239	40.21	40.73
21	....do	2680	20	1299	34.83	35.28
40	....do	3617	16	1233	44.69	....
41	....do	2004	15	1218	24.45	....
22	Iron	2961	20	0.01242	36.80	37.27
23	....do	2946	20	1275	37.57	38.05
24	....do	5071	20	1274	64.62	65.47
42	....do	4585	18	1209	55.55	56.60
43	....do	2409	18	1227	29.51	30.06
50	....do	5025	17	1222	61.70	62.86
51	....do	3791	17	1220	46.24	47.11
25	Chromium	2166	21	0.01314	28.47	28.84
26	....do	3294	21	1268	41.75	42.30
27	....do	3227	21	1314	42.41	42.96
44	....do	2652	15	1210	32.06	32.67
28	Tin	1714	21	0.01270	21.78	22.06
29	....do	1942	20	1337	25.97	26.30
30	....do	2961	20	1336	39.56	40.08
31	Aluminium	2001	20	0.01233	24.68	25.00
32	....do	1743	19	1265	22.04	22.33
33	Manganese	20.11	17	0.01298	26.11	26.45
34	....do	38.94	17	1287	50.11	50.76
35	Molybdenum	1273	16	0.01320	16.79	17.01
36	....do	1478	16	1298	19.18	19.43
45	....do	1438	15	1223	17.61	17.94
37	Lead	1211	16	0.01278	15.48	15.68
46	....do	1457	16	1212	17.68	18.01
38	Antimony	2200	18	0.01343	29.54	29.92
39	Bismuth	1223	19	0.01311	16.04	16.25
47	....do	1381	15	1200	16.60	16.91
52	Zinc	3894	14	0.01232	47.84	48.74
54	....do	1973	22	0.01261	24.75	25.21
53	Cadmium	1191	18	0.01254	15.0	....

EXPERIMENTAL DATA.

Further mechanical treatment resistance of wires.—Leaving the discussion and comparison of these results for the text below, I may state that the experiments were continued by rolling and drawing down the wires in a wire-plate to a mean diameter of about .046^{cm}. With these dimensions, the wires were manifestly well suited for a repetition of the resistance measurements just discussed under conditions thoroughly different from the above. In two respects, however, must the following results for specific resistance vary essentially from the former results. During the process of drawing the wires down from the larger section ($10^6\times q=12{,}000$ □cm) to the smaller section ($10^6\times q=1{,}200$ □cm), breakages are not always avoidable nor even unfrequent; hence, it is necessary to refuse and to work the metal over thoroughly. Thus it happens that certain metallic constituents are partially volatilized. Again, the thin and thick wires can not be identical in homogeneity in the way called for by the present measurement unless the thick wires were themselves thoroughly homogeneous at the outset, a condition not to be premised. Hence the data of Table 31, the symbols of which have the same signification as in Table 30, will not be rigorously identical.

The present data of resistance of thin wires are to be compared in the sequel with the thermo-electric and other data of the same wires. It is thus manifestly necessary to evaluate the respective constants of small lengths or parts of each of the wires. Inasmuch as all the data may be obtained accurately from less than 10cm of wire, and since for thermo-electric comparison only a mere point of this same partial length is necessary, it is obvious that the galvanic and thermo-electric constants may be obtained from a length of wire, the homogeneity of which may be assumed with impunity. For the total length being from 100cm to 200cm the efficient length is in every case less than one-tenth the length of the whole wire. It will be seen below that the stress I place on these results is by no means superfluous.

These remarks lead directly to Table 31.

TABLE 31.—*Electrical resistance of platinum alloys (thin wires).*

No.	Alloy.	r_t	t	$q\times10^6$	s_t
0	Platinum	12370	19	1257	15.55
0	....do				
1	Gold	18300	19	1439	19.13
2	....do	15620	19	1452	22.68
3	....do	17380	19	1452	25.23
4	Silver	13490	22	1466	19.78
5	....do	15450	22	1486	22.96
6	....do	22360	22	1548	34.61
7	Palladium	13170	22	1493	19.67
8	....do	14170	22	1520	21.54
9	....do	16490	22	1486	24.50
10	Iridium	13110	22	1534	20.11
11	....do	13740	22	1534	21.07
12	....do	15960	22	1520	24.26
13	Copper	20660	21	1562	32.27
14	....do	22000	21	1548	34.06
15	....do	40330	20	1576	63.56
48	... do	15160	23	1713	25.98
49	....do	31520	23	1706	53.78
16	Nickel	14170	22	1583	22.44
17	....do	17470	22	1576	27.54

TABLE 31.—*Electrical resistance of platinum alloys (thin wires)*—Continued.

No.	Alloy.	r_t	t	$q\times10^6$	s_t'
18	Nickel	21190	22	1576	33.38
19	Cobalt	18510	22	1576	29.17
20	....do	25560	22	1576	40.29
21	....do	19950	22	1590	31.72
40	....do	26400	23	1713	45.24
41	....do	14720	23	1676	24.68
22	Iron	23130	22	1590	36.78
23	....do	26620	23	1590	42.33
24	....do	37710	23	1598	60.28
42	....do	37510	23	1676	62.88
43	....do	17690	23	1662	29.39
50	....do	34870	23	1735	60.51
51	....do	28770	23	1735	49.91
25	Chromium	17600	23	1590	27.99
26	....do	26030	23	1590	41.39
27	....do	32670	23	1619	52.90
44	....do	....	......	....	....
28	Tin	13720	23	1619	22.21
29	....do	16090	22	1633	26.27
30	....do	24280	22	1662	40.35
31	Aluminium	15700	22	1655	25.98
32	....do	18220	22	1655	21.88
33	Manganese	15900	22	1655	20.31
34	....do	29900	22	1647	49.25
35	Molybdenum	9700	22	1720	16.68
36	....do	11840	22	1662	19.67
45	....do	....	......	....	....
37	Lead	8940	22	1720	15.37
46	....do	10510	23	1691	17.76
38	Antimony	17830	23	1691	30.14
39	Bismuth	....	......	....	....
47	....do	9890	23	1676	16.57
52	Zinc	26340	23	1691	44.55
54	....do	14890	23	1691	25.17
53	Cadmium	....	......	....	....
A	Platinum purified by three fusions (half an hour of melting in all).	710	23	1810	12.86
C		504	23	2781	14.02

Thermo-electrics of wires.—Having obtained this table in the way described, the marked ends of the wires were next subjected to thermo-electric measurement by exposing them to temperatures 100°, 358°, and 448°, respectively, in the boiling tubes, already fully described in Chapter II. The results are given in Table 32. "No." refers to the individual wires of the couple examined, and gives the sign of the two metals thermo-electrically combined. Thus Au(+1—0) denotes that the gold-alloy No. 1 is thermo-electrically positive to platinum No. 0. T and t are the temperatures of the thermo-electric junctions for which the electro-motive forces e (microvolts) apply, a and b the corresponding thermo-electric constants. Inasmuch as the thermo-electric data are necessarily most seriously affected by impurities in the alloys, it was deemed fully sufficient to compute *a* and *b* from extreme values for *t*, *T*, *e*, and then to test this computation with the intermediate value. Laborious applications of the method of least squares were therefore discarded.

TABLE 32.—*Thermo-electrics of platinum alloys.*

No.		*t*	*T*	*e* observed.	*e* calculated.	$10^3\times a$	$10^6\times b$
Au	+ 1−0	16	100	+ 46	+ 46	+ 540	+ 45
	+ 1−0	19	358	+ 185	+ 189		
	+ 1−0	17	448	+ 242	+ 242		
	+ 2−0	16	100	+ 155	+ 155	+ 1812	+ 263
	+ 2−0	19	358	+ 637	+ 648		
	+ 2−0	18	448	+ 832	+ 832		
	+ 3−0	17	100	221	221	+ 2570	+ 597
	+ 3−0	19	358	942	948		
	+ 3−0	18	448	1225	1225		
Ag	+ 4−0	18	100	7	7	+ 100	− 124
	+ 4−0	19	358	6	18		
	+ 4−0	18	448	18	18		
	+ 5−0	18	100	32	32	+ 436	− 412
	+ 5−0	22	358	88	94		
	+ 5−0	18	448	105	105		
	+ 6−0	18	100	107	107	+ 1301	− 7
	+ 6−0	22	358	428	436		
	+ 6−0	18	448	558	558		
Pd	− 7+0	18	100	− 86	− 86	− 844	−1738
	− 7+0	20	358	− 526	− 507		
	− 7+0	18	448	− 711	− 711		
	− 8+0	19	100	− 95	− 95	− 869	−2472
	− 8+0	20	358	− 631	− 600		
	− 8+0	18	448	− 869	− 869		
	− 9+0	19	100	− 120	− 120	− 1073	−3327
	− 9+0	20	358	− 821	− 788		
	− 9+0	19	448	−1127	−1127		
Ir	−10+0	19	100	− 222	− 222	− 2548	−1453
	−10+0	18	358	−1066	−1052		
	−10+0	19	448	−1384	−1384		
	−11+0	19	100	− 336	− 336	− 3904	−1799
	−11+0	18	358	−1584	−1557		
	−11+0	19	448	−2035	−2035		
	−12+0	19	100	− 517	− 517	− 5939	−3394
	−12+0	18	358	−2480	−2453		
	−12+0	19	448	−3228	−3228		
Cu	−13+0	18	100	− 15	− 15	− 77	−2212
	−13+0	18	358	− 271	− 257		
	−13+0	19	448	− 410	− 410		
	+14−0	18	100	+ 44	+ 44	+ 1021	−4139
	−14+0	18	358	− 250	− 190		
	−14+0	20	448	− 392	− 392		
	+15−0	19	100	+ 31	+ 31	+ 867	−4083
	+15−0	18	358	− 257	− 227		
	−15−0	20	448	− 447	− 447		
	−48+0	18	100	− 31	− 31	− 140	−2026

TABLE 28.—*Thermo-electrics of platinum alloys*—Continued.

No.		t	T	e observed.	e calculated.	10'×a	$10^6\times b$
Cu	—48+0	23	358	— 326	— 305		
	—48+0	19	448	— 466	— 466		
	+49—0	18	100	+ 41	+ 41	+ 915	—3483
	—49+0	23	358	+ 173	+ 138		
	—49+0	19	448	+ 305	+ 305		
Ni	—16+0	19	100	— 403	— 403	— 4905	— 333
	—16+0	18	358	—1734	—1710		
	—16+0	20	448	—2166	—2166		
	—17+0	19	100	— 745	— 745	— 9065	— 552
	—17+0	18	358	—3190	—3153		
	—17+0	20	448	—3990	—3990		
	—18+0	19	100	— 946	— 946	—11469	— 931
	—18+0	18	358	—4134	—4019		
	—18+0	20	448	—5095	—5095		
Co	+19—0	19	100	+ 89	+ 89	+ 1481	— 3294
	+19—0	19	358	+ 61	+ 81		
	+19—0	20	448	— 26	— 26		
	+20—0	19	100	+ 164	+ 164	+ 2560	— 4620
	+20—0	19	358	+ 253	+ 277		
	+20—0	20	448	+ 170	+ 170		
	+21—0	19	100	+ 186	+ 186	+ 3033	— 6276
	+21—0	19	358	+ 149	+ 226		
	+21—0	20	448	+ 41	+ 41		
	+40—0	19	100	+ 347	+ 347	+ 5519	—10290
	+40—0	20	358	+ 394	+ 551		
	+40—0	15	448	+ 327	+ 327		
	+41—0	19	100	+ 58	+ 58	+ 1038	— 2691
	+41—0	20	358	+ 18	+ 7		
	—41+0	16	448	+ 91	+ 91		
Iron	—22+0	19	100	— 382	— 382	— 3887	— 6772
	—22+0	15	358	—2226	—2200		
	—22+0	20	448	—3020	—3020		
	—23+0	19	100	— 402	— 402	— 3969	— 8058
	—23+0	15	358	—2401	—2392		
	—23+0	20	448	—3313	—3313		
	—24+0	19	100	— 438	— 438	— 4085	—11070
	—24+0	15	358	—2827	—2818		
	—24+0	21	448	—3962	—3962		
	—42+0	18	100	— 465	— 465	— 4222	— 1222
	—42+0	20	358	—2983	—2989		
	—42+0	16	448	—4274	—4274		
	—43+0	20	100	— 307	— 307	— 3246	— 4980
	—43+0	21	358	—1747	—1730		
	—43+0	18	448	—2393	—2393		
Steel	—50+0	18	100	— 474	— 474	— 4500	—11123
	—50+0	23	358	—2945	—2927		
	—50+0	19	448	4159	—4159		
	—51+0	19	100	— 368	— 368	— 3305	—10308
	—51+0	24	358	— 2383	—2419		
	—51+0	19	448	— 3483	—3483		

TABLE 28.—*Thermo-electrics of platinum alloys*—Continued.

No.		t	T	e observed.	e calculated.	$10^3\times a$	$10^6\times b$
Cr	−25+0	19	100	− 302	− 302	− 3211	− 4334
	−25+0	16	358	−1687	−1653		
	−25+0	21	448	−2239	−2239		
	−26+0	19	100	− 377	− 377	− 3733	− 7636
	−26+0	16	358	−2290	−2253		
	−26+0	21	448	−3123	−3123		
	−27+0	18	100	− 405	− 405	− 3766	− 9860
	−27+0	16	358	−2608	−2549		
	−27+0	21	448	−3583	−3583		
	−44+0	16	100	− 347	− 347	− 3494	− 5522
	−44+0	21	358	−1918	−1883		
	−44+0	19	448	−2605	−2605		
Sn	−28+0	19	100	− 30	− 30	− 287	− 691
	−28+0	17	358	− 194	− 186		
	−28+0	20	448	− 261	− 261		
	−29+0	18	100	− 16	− 16	− 10	− 771
	−29+0	17	358	− 146	− 134		
	−29+0	20	448	− 199	− 199		
	+30−0	18	100	+ 16	+ 16	+ 378	− 1562
	−30+0	17	358	− 99	− 71		
	−30+0	19	448	− 151	− 151		
Al	−31+0	18	100	− 102	− 102	− 1050	− 1641
	−31+0	17	358	− 594	− 568		
	−31+0	19	448	− 779	− 779		
	−32+0	19	100	− 130	− 130	− 1398	− 1688
	−32+0	18	358	− 706	− 691		
	−32+0	19	448	− 938	− 938		
Mn	−33+0	17	100	− 90	− 90	− 869	− 1925
	−33+0	19	358	− 564	− 541		
	−33+0	20	448	− 758	− 758		
	−34+0	17	100	− 253	− 253	− 2360	− 5957
	−34+0	19	358	−1671	−1561		
	−34+0	19	448	−2206	−2206		
Mo	−35+0	17	100	− 36	− 36	− 378	− 504
	−35+0	19	358	− 202	− 193		
	−35+0	19	448	− 263	− 263		
	−36+0	18	100	− 275	− 275	− 3170	− 1660
	−36+0	19	358	−1320	−1287		
	−36+0	25	448	−1673	−1673		
	−45+0	17	100	− 119	− 119	− 1312	− 1014
	−45+0	22	358	− 557	− 570		
	−45+0	19	448	− 766	− 766		
Pb	+37−0	19	100	+ 43	+ 43	− 503	− 264
	+37−0	20	358	+ 208	+ 204		
	+37−0	20	448	+ 268	+ 268		
	−46+0	18	100	− 50	− 50	− 549	− 510
	−46+0	22	358	− 258	− 248		
	−46+0	22	448	− 338	− 338		
Sb	−38+0	19	100	− 131	− 131	− 1261	− 3073
	−38+0	20	358	− 840	− 819		
	−38+0	20	448	−1155	−1155		

TABLE 28.—*Thermo-electrics of platinum alloys*—Continued.

No.		t	T	e observed.	e calculated.	$10^3 \times a$	$10^6 \times b$
Bi	−47+0	18	100	− 39	− 39	− 443	− 274
	−47+0	22	358	− 188	− 184		
	−47+0	19	448	− 245	− 245		
Zn	+52−0	19	100	+ 18	+ 18	+ 612	− 3288
	−52+0	24	358	− 248	− 215		
	−52+0	19	448	− 396	− 396		
	+54−0	19	100	+ 19	+ 19	+ 296	− 514
	+54−0	24	358	+ 18	+ 33		
	+54−0	19	448	+ 24	+ 24		

Temperature-coefficient.—Table 33 contains the final series of data relative to the pyrometric constants of these wires. It contains mean values of the relation α between electrical resistance and temperature for each of the 52 wires of the above table. The marked ends of these, having been wrapped around the little insulating cylinders of porcelain so as to form a helix, the platinum spires of which do not touch each other ("open spiral spring"), were exposed to 25°, to 100°, and to 358°, respectively, in the space of constant temperature of my boiling tubes. To retain the helix, which is never more than 2^{cm} long along its axis, in place, and likewise to connect the terminals of the bridge adjustment with it, the ends of the helix wire are fused to terminals of fairly-thick copper wire. One of these terminals passes through one canal of the porcelain insulator to connect with the upper end of the platinum helix, the other terminal partially through the second canal in a suitable way to connect with the lower end of the helix. The measurements are then made in the customary way. Constancy of temperature along the 2^{cm} of length of helix may be assumed. The total length of platinum wire in the helix is that for which the above data, Table 31, apply.

In Table 33 therefore r_t is the resistance corresponding to the temperature T, and α_0^{100}, α_0^{360} are the mean temperature-coefficients for the intervals of temperature 0° to 100° and 0° to 360°, respectively.

TABLE 33.—*Temperature-coefficients of platinum alloys.*

	No.	T	r_t	$10^3 \times \alpha_0^{100}$	$10^3 \times \alpha_{100}^{360}$
Pt ..	0	25	0.759	2.30	2.22
	0	100	0.883		
	0	357	1.296		
Au ..	1	20	0.408	1.78	1.62
	1	100	0.464		
	1	357	0.630		
	2	21	0.485	1.46	1.33
	2	100	0.539		
	2	357	0.702		
	3	22	0.542	1.27	1.09
	3	100	0.594		
	3	357	0.744		

TABLE 33.—*Temperature-coefficients of platinum alloys*—Continued.

	No.	T	r_t	$10^3 \times \alpha_0^{100}$	$10^3 \times \alpha_{100}^{350}$
Ag..	4	23	0.413	1.80	1.61
	4	100	0.468		
	4	357	0.635		
	5	25	0.472	1.46	1.02
	5	100	0.522		
	5	357	0.675		
	6	25	0.631	1.02	0.71
	6	100	0.678		
	6	357	0.794		
Pd..	7	19	0.408	1.75	1.62
	7	100	0.464		
	7	357	0.630		
	8	19	0.441	1.53	1.48
	8	100	0.494		
	8	357	0.658		
	9	19	0.501	1.29	1.18
	9	100	0.552		
	9	357	0.701		
Ir ..	10	19	0.408	1.72	1.61
	10	100	0.463		
	10	357	0.628		
	11	18	0.425	1.63	1.50
	11	100	0.480		
	11	357	0.641		
	12	18	0.495	1.28	1.21
	12	100	0.546		
	12	357	0.697		
Cu..	13	18	0.640	0.89	0.83
	13	100	0.686		
	13	357	0.821		
	14	18	0.678	0.80	0.72
	14	100	0.722		
	14	357	0.847		
	15	18	1.205	0.20	0.20
	15	100	1.225		
	15	357	1.286		
Ni..	16	17	0.443	1.68	1.46
	16	100	0.503		
	16	357	0.668		
	17	17	0.506	1.34	1.19
	17	100	0.561		
	17	357	0.714		
	18	18	0.673	1.05	0.87
	18	100	0.730		
	18	357	0.880		
Co..	19	18	0.572	1.09	1.04
	19	100	0.622		
	19	357	0.772		

TABLE 33.—*Temperature-coefficients of platinum alloys*—Continued.

	No.	T	r_t	$\alpha_0^{100} \times 10^3$	$\alpha_{100}^{350} \times 10^3$
Co..	20	20	0.783	0.89	0.74
	20	100	0.838		
	20	357	0.966		
	21	20	0.639	1.57	1.30
	21	100	0.717		
	21	357	0.929		
Fe..	22	21	0.708	0.74	0.74
	22	100	0.749		
	22	357	0.892		
	23	21	0.797	0.66	0.64
	23	100	0.838		
	23	357	0.968		
	24	21	1.405	0.37	0.36
	24	100	1.446		
	24	357	1.575		
Cr..	25	21	0.536	1.14	1.06
	25	100	0.583		
	25	357	0.726		
	26	21	0.791	0.65	0.62
	26	100	0.831		
	26	357	0.956		
	27	21	0.963	0.56	0.49
	27	100	1.005		
	27	357	1.125		
Sn..	28	20	0.392	1.55	1.40
	28	100	0.439		
	28	357	0.585		
	29	19	0.497	1.27	1.20
	29	100	0.547		
	29	357	0.697		
	30	19	0.848	0.69	0.66
	30	100	0.895		
	30	357	1.038		
Al..	31	15	0.489	0.85	1.32
	31	100	0.524		
	31	357	0.681		
	32	16	0.408	1.56	1.50
	32	100	0.460		
	32	357	0.614		
Mn..	33	17	0.488	1.28	1.14
	33	100	0.539		
	33	357	0.680		
	34	18	0.946	0.52	0.43
	34	100	0.986		
	34	357	0.091		
Mo.	35	19	0.302	2.13	1.94
	35	100	0.352		
	35	357	0.499		
	36	19	0.370	1.76	1.69
	36	100	0.421		
	36	357	0.577		

TABLE 33.—*Temperature-coefficients of platinum alloys*—Continued.

	No.	T	r_t	$a_0^{100}\times 10^3$	$a_{100}^{357}\times 10^3$
Pb..	37	20	0.298	2.28	2.23
	37	100	0.350		
	37	357	0.514		
Sb..	38	20	0.541	1.11	1.09
	38	100	0.588		
	38	357	0.736		
Co..	40	21	0.810	1.30	0.83
	40	100	0.891		
	40	357	0.067		
Co.	41	22	0.456	1.39	1.27
	41	100	0.504		
	41	357	0.650		
Fe.	42	22	1.098	0.44	0.39
	42	100	1.135		
	42	357	1.243		
	43	23	0.345	1.12	0.98
	43	100	0.374		
	43	357	0.460		
Cr.	44	20	0.591	0.95	0.87
	44	100	0.635		
	44	357	0.766		
Mo.	45	20	0.227	2.06	1.88
	45	100	0.263		
	45	357	0.370		
Pb.	46	20	0.225	2.02	1.82
	46	100	0.260		
	46	357	0.363		
Bi.	47	20	0.303	2.10	2.03
	47	100	0.352		
	47	357	0.505		
Cu.	48	19	0.467	1.27	1.14
	48	100	0.514		
	48	357	0.648		
	49	19	0.978	0.29	0.15
	49	100	1.001		
	49	357	1.038		
Fe.	50	19	0.771	0.44	0.39
	50	100	0.798		
	50	357	0.875		
	51	19	0.815	0.77	0.64
	51	100	0.865		
	51	357	0.999		
Zn.	52	15	0.840	0.51	0.32
	52	100	0.876		
	52	357	0.945		
	54	18	0.391	1.34	1.14
	54	100	0.433		
	54	357	0.547		

PURIFIED WIRES.

A. Thrice fused.	19 100 357	0.223 0.273 0.420	2.90	2.65
C. Thrice fused.	19 100 357	0.299 0.357 0.545	2.52	2.58

General digest.—Following, in Table 34, is a general digest of the above results, in which density Δ_0 at zero degrees, specific resistance s_t, as obtained from thick (I) and from thin (II) wires at mean room temperatures, mean temperature-coefficient α for the large and the small intervals 0° to 100° and 0° to 360°, respectively, specific resistance s_0 for 0° computed with α, and, finally, the thermo-electric power a per degree centigrade at 0°, are carefully inserted. The data for purified wires are discussed below:

TABLE 34.—*Constants of platinum alloys. Digest.*

No.	Metal alloyed to platinum.	Δ_0	I (thick) s_t	II (thin) s_t	$10^3\times\alpha$		II (thin) s_0	$10^3\times a$	$[f'(0):f(0)]\times 10^3$
0	Platinum	21.315	15.30	15.55	2.30	2.22	14.91	....	2.33
1	Gold..............	21.288	18.98	19.13	1.78	1.62	18.53	540	1.84
2	....do	21.221	22.44	22.68	1.45	1.33	22.13	1812	1.49
3	....do	21.172	25.58	25.23	1.27	1.09	24.67	2570	1.33
4	Silver	21.163	19.48	19.78	1.80	1.61	19.06	100	1.87
5	....do	20.991	22.79	22.96	1.46	1.02	22.28	436	....
6	....do	19.400	34.80	34.61	1.02	0.71	33.97	1301	....
7	Palladium	21.006	19.53	19.67	1.75	1.62	18.95	− 844	1.79
8	.... do	20.540	21.40	21.54	1.53	1.48	20.90	− 869	1.55
9	....do	19.909	23.86	24.50	1.29	1.18	23.87	− 1073	1.33
10	Iridium...........	21.271	19.87	20.11	1.72	1.61	19.42	− 2548	1.76
11	....do	21.279	21.17	21.07	1.63	1.50	20.40	− 3904	1.67
12	....do	21.319	24.43	24.26	1.28	1.21	23.64	− 5939	1.30
13	Copper	20.676	31.51	32.27	0.89	0.83	31.75	− 77	0.91
14	....do	20.600	33.97	34.06	0.80	0.72	33.59	1021	0.83
15	....do	18.803	63.82	63.56	0.20	0.20	63.56	867	0.21
48	....do	20.917	25.69	25.98	1.27	1.14	25.29	− 140	1.31
49	....do	19.561	55.87	53.78	0.29	0.15	53.60	915	0.34
16	Nickel............	20.686	21.93	22.44	1.68	1.46	21.67	− 4905	1.75
17	....do	19.889	27.51	27.54	1.34	1.19	26.84	− 9065	1.39
18	.. do	18.751	33.71	33.38	1.05	0.87	32.76	−11470	1.11
19	Cobalt............	20.590	30.01	29.17	1.09	1.04	28.56	1481	1.11
20	....do	19.841	40.21	40.29	0.89	0.74	39.62	2560	0.93
21	....do	19.329	34.83	31.72	1.57	1.30	30.70	3033	....
40	....do	19.100	44.69	45.24	......	0.83	44.57	5519	....
41	....do	20.992	24.45	24.68	1.39	1.27	23.97	1038	1.43
22	Iron	20.628	36.80	36.78	0.74	0.74	36.33	− 3887	0.74
23	....do	20.330	37.57	42.33	0.66	0.64	41.80	− 3969	0.67
24	...do	19.580	64.62	60.28	0.37	0.36	59.92	− 4085	0.37
42	....do	19.750	55.55	62.88	0.44	0.39	62.52	− 4222	0.46
43	....do	20.886	29.51	29.30	1.12	0.98	28.75	− 3246	1.21
50	Steel..............	19.581	61.70	60.51	0.44	0.39	60.16	− 4500	0.46

TABLE 34.—*Constants of platinum alloys. Digest*—Continued.

No.	Metal alloyed to platinum.	Δ_0	I (thick) s_t	II (thin) s_t	$10^3\times\alpha$		II (thin) s_0	$10^3\times a$	$[f'(0):f(0)]\times10^3$
51	....do	19.952	46.24	49.91	0.77	0.64	49.16	− 3305	0.81
25	Chromium	20.911	28.47	27.99	1.14	1.06	27.37	− 3211	1.17
26	....do	20.512	41.75	41.39	0.65	0.62	40.87	− 3738	0.66
27	....do	20.157	42.41	52.90	0.56	0.49	52.35	− 3766	0.58
44	....do	20.764	32.06	31.71	0.95	0.87	31.09	− 3494	0.98
28	Tin	21.109	21.78	22.21	1.55	1.49	21.52	− 287	1.57
29	....do	20.974	25.97	26.27	1.27	1.20	25.60	− 10	1.29
30	....do	20.449	39.56	40.35	0.69	0.66	39.86	+ 378	0.70
31	Aluminium	20.464	24.68	25.98	......	1.32	25.33	− 1050	....
32	....do	20.724	22.04	21.88	1.56	1.50	21.18	− 1398	1.58
33	Manganese	20.807	26.11	26.31	1.28	1.14	25.64	− 869	1.33
54	....do	19.433	50.11	49.25	0.52	0.43	48.87	− 2360	0.55
35	Molybdenum	21.263	16.79	16.68	2.13	1.94	15.96	− 879	2.29
36	....do	21.261	19.18	19.67	1.76	1.69	18.95	− 3170	1.78
45	....do	21.302	17.61	17.17	2.06	1.88	16.40	− 1312	2.12
37	Lead	21.180	15.48	15.37	2.28	2.23	14.64	− 503	2.30
46	....do	21.241	17.68	17.76	2.02	1.82	17.00	− 550	2.09
38	Antimony	20.753	29.54	30.14	1.11	1.09	29.48	− 1261	1.12
39	Bismuth	21.179	16.04	....	......	......	....	....	....
47	....do	21.329	16.60	16.57	2.10	2.03	15.83	− 443	2.12
52	Zinc	20.102	47.84	44.55	0.51	0.32	44.19	+ 612	0.57
54	....do	20.975	24.75	25.17	1.34	1.14	24.51	+ 296	1.41
53	Cadmium	(21.3)	15.00	....	......	......	....	....	....

PURIFIED WIRES

A. Thrice fused.	Platinum	....	....	12.86	2.90	2.65	12.04	....	2.96
C. Thrice fused.	....do	....	....	14.02	2.52	2.58	13.27	....	2.50

DISCUSSION AND INFERENCES.

Earlier results.—I shall pass rapidly over the above data for density resistance and thermo-electric behavior, since they are frequently provisional. They exhibit a definite method of work carried to an issue. The results are of increasing value in proportion as they lead to the relation between electrical resistance and temperature-coefficient of electrical resistance, to which I have already adverted.

Here I may state that the original attempts to co-ordinate resistance and thermo-electric power were made by Dr. Strouhal and myself[1] in discussing data for steel. The striking success of this attempt, to which a large number of subsequent results gave additional and final warranty, led us naturally to seek for similar relations in alloys of one metal with consecutive small parts of a second metal. These results,

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[1] Cf. Wied. Ann., vol. 7, 1879, p. 383; ibid, 1880, vol. 11, p. 930.

however, exhibit more complicated relations. Indeed, our data for alloys of silver with platinum, gold, copper, and zinc showed that the results for steel were due to causes intrinsically different from the causes varying the electrical properties of alloys. Owing partially to this negative result and partially to the necessity of changing our laboratory location from Würzburg to Prague and to Washington, these data[1] for alloys remained unpublished in German until 1884, and in English[2] until 1885.

In the mean time M. L. Weber,[3] who, at the suggestion of Beetz, had sought for similar relations among the amalgams of mercury, was able to publish a fine and elaborate research on the galvanics and thermoelectrics of those substances. In addition to the results of Strouhal and myself for silver alloys, and Weber's results for amalgams, it was hoped that the present results for platinum alloys would supply such a sufficiency of new data that from all the results thus in hand certain general inferences bearing on the properties of alloys might safely be drawn. This discussion must, however, be deferred for the reasons already mentioned, page 125.

Resistance and density.—Turning first to the columns for Δ_0, s_t I, and s_t II, in Table 34, the number of strikingly large values of the specific resistance of platinum alloys at once meets the eye. If the specific resistance of good commercial platinum be put $s_t=13$, then it needs but trifling additions of chromium, or iron, or copper, or tin, or manganese, or zinc, etc., to increase this resistance nearly fivefold. In discussing results for silver alloys Dr. Strouhal and I observed that the galvanic effect produced by alloying increased with the differences of density of the ingredients of the alloy. In view of the exceptionally high density of platinum and the pronounced tendency of this metal to form alloys of high specific gravity, these inferences seem to be substantiated here, bearing in mind that the differences of density of the ingredients can only be one of many factors which go to determine the properties of the alloy produced. To go into further particulars is undesirable, but I may remark that though the effect produced by aluminium is exceptionally small, iridium and gold, both of large densities, produce small increments of resistance, whereas the enormous variations due to tin, chromium, iron, zinc, copper, manganese, cobalt, silver, nickel, palladium, decrease in general in the order of their increasing densities. The absorption of gases, the want of homogeneity, and the very probable tendency to form alloys of definite chemical composition are the main causes which tend to obscure the regularity of the physical phenomena. The differences between s_t I and s_t II, derived, respectively, from the bars and the wires, are no larger than may be easily referred to difficulties of manipulation. In the case of chromium, of iron, of cobalt, and of aluminium

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[1] Abh. königl. Böhm. Gesell. Wiss., 6th series, vol. 12, 1884.

[2] Bull. U. S. Geol. Survey, No. 14, 1885, pp. 76 to 88.

[3] Weber: Wied. Ann. vol. 23, 1884, p. 447.

alloys, large discrepancies sometimes occur, showing that in these instances the base metal can not have been perfectly dissolved nor the alloy satisfactorily homogeneous. Inasmuch, however, as the method of comparing the specific resistance of the ingot as a whole, as it were, with a small part of the wire drawn from it is a very rigorous test for the homogeneity of the alloy, it appears from the coincidence of the results for s_t I and s_t II, that melted platinum may indeed be regarded as a solvent for metals generally. The importance of this quality has already been signalized above.

Resistance and thermo-electrics.—It has been stated that the thermo-electric results are the ones most influenced by impurities in the platinum, for the alloys of this metal, though exhibiting enormous differences of resistance, are, with few exceptions, relatively without marked thermo-electric variability. This is an observation of importance, particularly if considered with reference to the position of the individual alloys in the series. It shows that there is probably no intrinsic relation whatever between specific resistance and thermo-electric power when the variations of both the quantities are produced by alloying. Curiously enough the extremes of the thermo-electric variations are the cobalt and the nickel alloys, the former being powerfully positive, the latter even more powerfully negative. The iridium alloy has the well-known extreme electro-negative position, as would also have the molybdenum alloys. On the other hand, the positions of iron, of chromium, of manganese are not nearly as extreme as would have been anticipated from their resistance values, whereas the powerfully resisting combinations of platinum-copper, platinum-zinc, platinum-tin show only insignificant values of thermo-electric power. In short, there appears to be no law for the co-ordination of the galvanic and thermo-electric qualities discernible, and large values in the one case by no means imply large values in the other.

Electrical tests for purity.—Having thus briefly discussed the thermo-electric and resistance data in the above tables, it will be next in place to describe the experiments made to ascertain the condition of purity of the platinum used. These experiments have special importance, because they exhibit the electrical behavior of commercial platinum frequently treated before the oxyhydrogen blow-pipe, and therefore show what degree of purity of platinum is necessary in order that the metal may be safely used practically in thermo-electric temperature measurement.

The original experiments made with a length marked A, and cut from the coil above described, behaved in such a way as to give rise to no serious apprehensions. This piece was first annealed, and then thermo-electrically combined with No. 0, as were the wires in Table 32.

The following data were obtained, nomenclature as above:

TABLE 35.—*Electrical tests for purity.*

Number.	t	T	e observed.	e calculated.	$a \times 10^3$	$b \times 10^6$
$+A-0$...	20	100	+ 68	68	....	....
$+A-0$...	18	358	+345	335	777	554
$+A-0$...	17	448	+447	446	....	....

This wire A was then fused before the oxyhydrogen blow-pipe consecutively for five minutes each time and tested both for resistance and for thermo-electric power after each fusion. The results investigated range as follows, being obtained, of course, from wires drawn and softened from the buttons, for each case:

TABLE 36.—*Electrical tests for purity.*

Treatment.	Galvanics.				Thermo-electrics.		
	r_t	t	$q \times 10^6$	s_t	Couple.	$T-t$	e
Before fusion......	913	23	1450	13.5	$+A-0$....	358—25	+336
After one fusion...	707	23	1890	13.3	$+A-0$....	358—25	+347
After two fusions..	723	23	1810	13.1	$+A-0$....	358—25	+337
After three fusions.	710	23	1810	12.9	$+A-0$....	358—25	+345

These results give clear evidence of the occurrence of volatilization during the whole of the fifteen minutes of fusion before the blow-pipe. But the amount of variation (6 per cent.), though large in itself, was not relatively so large with reference to the total variation due to alloying (500 per cent.) as to be seriously apprehended. Moreover, the button could be purified by intensely fusing it on lime for some time before alloying it.

A second set of experiments, unfortunately made some time after these, gave rise to much more pronounced results. To determine the degree of homogeneity of the wire I compared parts of it of about 100^{cm} each, the original positions of which were about equidistant along the whole 130 meters of platinum wire. The galvanics and thermo-electrics of these samples ranged as follows, each having been softened before testing:

TABLE 37.—*Electrical tests for purity.*

No.	Galvanics.				No.	Thermo-electrics.		
	r_t	t	$q \times 10_6$	s_t		t	T	e
B	1115	23	1493	16.7	$-B+0$	25	358	—127
C	1220	23	1493	18.2	$-C+0$	25	358	—358
D	1198	23	1493	17.9	$-D+0$	25	358	- 386
E	1185	23	1493	17.7	$-E+0$	25	358	—284
F	1058	23	1493	15.8	$+F-0$	25	358	+18
					$-C+A$	25	358	—691

These wires, *B*, *C*, *D*, *E*, *F*, were now fused thoroughly together and kept melted before the blow-pipe for fifteen minutes; thereupon drawn, annealed, and softened. The new wire on being tested gave the following results:

TABLE 38.—*Electrical tests for purity.*

No.	Galvanics.				No.	Thermo-electrics.		
	r_t	t	$q\times10^6$	s_t		t	T	e
$(B+C+D+E+F)$	786	23	1964	15.4	$-(B+C+D+E+F)+0$	25	358	−241

The new wire was now again purified by fusing for fifteen minutes; then drawing and annealing. The results obtained were:

TABLE 39.—*Electrical tests for purity.*

No.	Galvanics.				No.	Thermo-electrics.		
	r_t	t	$q\times10^6$	s_t		t	T	e
$(B'+C'+D'+E'+F')$	504	23	2781	14.0	$-(B'+C'+D'+E'+F')+0$	25	358	−170

The direct result for e in case of the couple $-C+A$ agrees well with the result which may be compounded from Tables 35 and 37. If now we compare the mean values of s_t from Table 37 (17.3) and the values in Tables 38 and 39 (15.4, 14.0), it appears that the decrement or volatilization of the impurity is greatest during the first minutes of the fusion. Hence, since it was customary to heat the buttons beyond the fusing point for several minutes before alloying, and since, moreover, the range of specific resistances due to alloying is enormously large, it is probable that impurities in the platinum have not distorted the data for resistance and density to a serious extent.

The same degree of reliance can not be placed on the thermo-electric data. Indeed, the behavior of the fused sample here is curious. In Table 36, for instance, the values of e oscillate, and are actually greater after the third fusion than originally, whereas the values of s_t for the same wire, under the same circumstances, decrease with the utmost regularity. The mean values of Table 37, as compared with the values in Tables 38 and 39, show a similar irregularity of decrease. It follows therefore that the results for $a\times10^3$ must be regarded as distorted by an arbitrary constant, which remains nearly the same for a single set of alloys, but which varies from one set to another by an amplitude, the maximum total value of which can not be safely put less than 1,000. In other words, the error of $a\times10^3$ from series to series may be as large as ±500. It is only the more powerful thermo-electric combinations in the above, *i. e.*, alloys of gold, cobalt, silver, manganese, chromium, iron, nickel, iridium, and molybdenum, which fall well outside of this zone of error, and for such only have thermo-electric inferences been drawn.

Electrical resistance and its temperature-coefficient.—I have now to touch upon the main results of the present chapter, *i. e.*, the relation between the resistance (s_0) and the temperature-coefficient of resistance (α). The results in the digest, Table 34, may be best exhibited in a chart, Fig. 26, in which $\alpha \times 10^3$ is represented as a function of s_0. It is well to remark in passing that α has been calculated by a linear formula, and from the three observations made at ordinary temperatures at 100° and at 357° two values of α may be reasonably deduced, since the measurement at room temperature is less liable to error. The equation $\alpha=(r-r')\,/\,(rt'-rt')$ furnishes α_0^{100} and α_0^{356}, both of which are inserted in Table 36. s_0 applies for 0° C. The assumption of the linear form has been wholly a matter of convenience, it being desirable to avoid the excessive computation which would have been necessitated by quadratic forms.

The figure contains both α_0^{100} and α_0^{356}, the former of which is given in heavy or large dots; the latter is in comparatively light dots. Vertical lines pass through each datum, and at their ends the name of the platinum alloy is inscribed. For the sake of comparison, finally, there has been introduced into the chart a curve showing the results which Dr. Strouhal and I[1] formerly obtained for iron-carburets, the data themselves ranging as follows:

Specific electrical resistance and electrical temperature-coefficient of steel. Practical table.

s	a	s	a	s	a	s	a
$\frac{\text{cm}}{\text{cm}^2}\,0^\circ$ *microhm.*		$\frac{\text{cm}}{\text{cm}^2}\,0^\circ$ *microhm.*		$\frac{\text{cm}}{\text{cm}^2}\,0^\circ$ *microhm.*		$\frac{\text{cm}}{\text{cm}^2}\,0^\circ$ *microhm.*	
10	0.0050	21	0.0033	32	0.0022	43	0.0017
11	48	22	32	33	21	44	17
12	46	23	31	34	21	45	16
13	44	24	20	35	21	46	16
14	42	25	28	36	20	47	15
15	41	26	27	37	19	48	15
16	39	27	27	38	19	49	15
17	38	28	26	39	19	50	15
18	36	29	25	40	18	60	13
19	35	30	24	41	18	70	13
20	34	31	23	42	17	80	12

This curve is dotted in the figure, the alloy curve being given in a full line.

Returning to the curve for alloys, it appears that the difference between α_0^{100} and α_0^{356} is not larger than is quite in keeping with the occurrence of reasonable curvilinear relations between resistance and temperature, and that for the present purposes, where a general survey over the whole group of platinum alloys is to be attempted, α_0^{100} may be accepted as coincident in value with the respective tangents of the

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[1] Wied. Ann., vol. 20, 1883, p. 525; Bull. U. S. Geol. Survey, No. 14, 1885, p. 19.

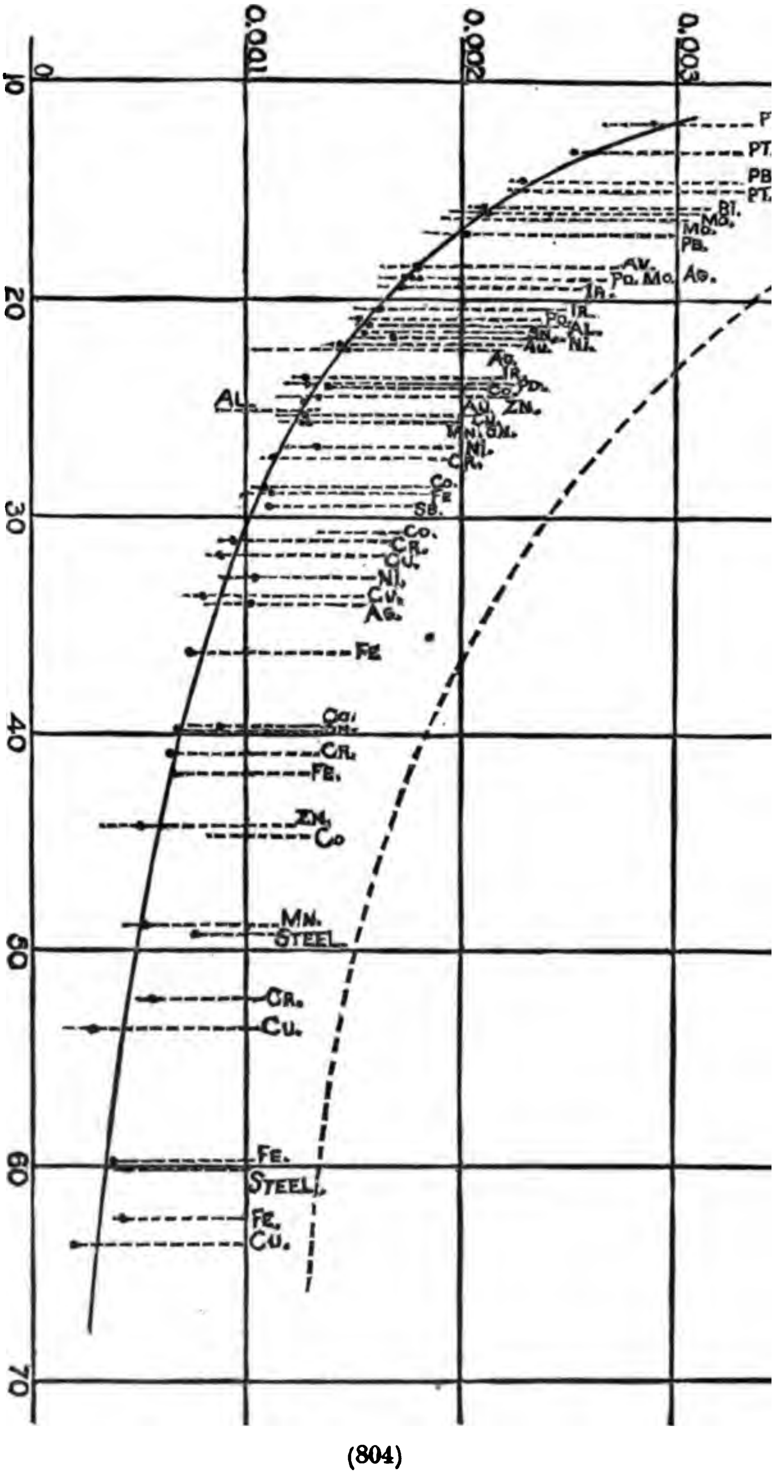

Fig. 26. Chart showing the relation between electrical resistance (microhms) and temperature-coefficient of platinum alloys.

curvilinear relations in question. Large differences between α_0^{100} and α_0^{356} occur in case of one aluminium alloy, two cobalt alloys, and one silver alloy; but the exceptional data of the aluminium alloy, as well as the cobalt alloys, have already been adverted to above in discussing the density and resistance data. In the case of the aluminium alloy, I suspect that some error of measurement has eluded me, whereas the two cobalt alloys seem to be deficient in homogeneity, as is also the silver alloy. These inferences are permissible, because the remaining aluminium, cobalt, and silver alloys behave normally, and I am therefore warranted in excluding the three unmistakably exceptional data (Al, Co, Co) from the present considerations altogether.

Without any essential restrictions therefore I need only fix attention upon the large black dots of the chart, and from these 52 data it appears clearly that the alloys of platinum may be regarded as a class of materials possessing certain generic physical properties, inasmuch as the effect of alloying platinum with small amounts (less than 10 per cent.) of any other metal is a variation of the limiting ratio of resistance and temperature, when the latter approaches zero, in a way that is independent of the special ingredients of the alloy from which data may be obtained. Such variation depends only on the resistance-position of this alloy in the class.

In other words, if I put $s_t = f(t)$, where f is a series of powers of t then $s_0 = f(0)$ and $\alpha = f'(0) : f(0)$, and therefore s_0 and α, considered theoretically, have to each other relations expressible by a first differential coefficient. According to the experimental result just stated, furthermore, $f'(0) : f(0)$ is such a function of $f(0)$ that the dependence of $f'(0) : f(0)$ on $f(0)$ is independent of the ingredients of the alloy by which the variations of $f(0)$ may be produced, provided, of course, the point of view be that of obtaining a broad class distinction for the platinum alloys as a whole, and not to discern rigorously the characteristics of the individual alloy. To return again to the figure with a view of examining the discrepancies critically, I find that the divergence of data from the mean curve, drawn as carefully as possible through them, is largest toward the right-hand half of the figure. This, however, is easily accounted for, since in proportion as the resistance of the alloy is greater the results are more and more seriously distorted by an insufficiently homogeneous mixture or by imperfect alloying of the ingredients of the metal. The alloys of nickel, perhaps, are conspicuous as occupying a position above the mean curve, the alloys of copper as falling below it, but for the other alloys a uniformly exceptional position can not be said to be discernible. If the alloying be imperfect the corresponding α will be erroneously large, and a tendency toward over-large values of α is the general character of the discrepancies which the figure presents.

Probably, too, the extreme end of the curve already partakes of the divergence, in virtue of which, in a retrograde movement, the diagram position of the metal alloyed to platinum must ultimately be reached.

Having therefore obtained some general notions of the dependence of $f'(0):f(0)$ on $f(0)$, it is next in place to endeavor to inquire into the form of dependence of these two classes of experimental data on each other. With a view of arriving at as simple a relation as possible I have tested the hyperbolic equation—

$$(f(0)+l)(f'(0):(f(0)+m)=n \quad \ldots\ldots\ldots \quad (1)$$

which contains three constants, and for the computation of which three pairs of values of $f(0)$ and $f'(0):f(0)$ suffice. These may be taken from the figure, with some care as regards the judicious selection of points, as follows:

$$\begin{array}{rr} f(0)=11.7 & f'(0):f(0)\ 0.00300 \\ 20.0 & 0.00164 \\ 50.0 & 0.00050 \end{array}$$

If we denote $f(0)$ and $f'(0):f(0)$ for a moment by x and y, the values of l and m have the general forms

$$l=\frac{(x-x'')(xy-x'y')-(x-x')(xy-x''y'')}{(y-y'')(x-x')-(x-x'')(y-y')} \quad \ldots\ldots \quad (2)$$

$$m=-\frac{(y-y'')(xy-x'y')-(y-y')(xy-x''y'')}{(y-y'')(x-x')-(x-x'')(y-y')} \quad \ldots\ldots \quad (3)$$

which, together with equation (1) for the special values of x and y, lead to the constants

$$l=-0.1360 \qquad m=0.0002548 \qquad n=0.03764.$$

Moreover, the curve

$$(f(0)-0.1360)(f'(0):f(0)+0.0002548)=0.03764 \quad \ldots \quad (4)$$

does not differ appreciably from the curved line which, in Fig. 26, has been accepted as the locus of the larger black dots.

Equation (4), however, is exceedingly significant. Inasmuch as $f(0)$ varies between 10 and 70, l is generally considerably less than 1 per cent. of $f(0)$. Equation (4) therefore emphatically suggests that a *simpler* form of equation be assumed, in which $l=0$. Equation (4), however, contains still another striking suggestion. The positive character of the constant m indicates that a larger value than α_0^{100}, or the mean temperature-coefficient between zero and 100°, will tend to further simplify equation (4). Now, since, generally, $\alpha_0^{100}>\alpha_0^{356}$, it follows that

$$f'(0):f(0)=\alpha>\alpha_0^{100}.$$

Hence, with these modifications implied,

$$f(0)(f'(0):f(0)+m)=n \quad \ldots\ldots\ldots \quad (5)$$

will in all probability hold good for the observations as a whole even more nearly than (4).

To avoid complete recalculation of α it is desirable to investigate some method for passing from α_0^{100} and α_0^{357} to α. If the values

s, s', s'' correspond to t, t', t'',

and if I accept

$$\frac{s}{1+\alpha t+\beta_t^2}=\frac{s'}{1+\alpha t'+\beta_t'^2}=\frac{s''}{1+\alpha t''+\beta_t''^2}$$

there follows:

$$\alpha=\frac{(s'-s)(st''^2-s''t^2)-(s''-s)(st'^2-s't^2)}{(st'-s't)(st''^2-s''t^2)-(st''-s''t)(st'^2-s't^2}$$

from which it is easy to deduce

$$\alpha-\alpha_0^{100}=\frac{\alpha_0^{100}-\alpha_0^{356}}{\dfrac{st''^2-s''t^2}{st''-s''t}\Big/\dfrac{st'^2-s't^2}{st'-s't}-1}$$

Now, $st''-s''t=D''$ and $st'-s't=D'$ are already known from the earlier computations; and for the present purpose, where a correction only is sought, $s''t^2$ and $s't^3$ may be neglected as compared with st''^3 and st'^2, respectively, t being small in comparison with t' and t''. Hence

$$\alpha-\alpha_0^{100}=\frac{\alpha_0^{100}-\alpha_0^{356}}{\dfrac{t''^2\,D'}{t'^2\,D''}-1}$$

which, since t''_2/t'^2 is a constant, is a sufficiently convenient form, and much of the correcting may be done mentally. Finally, the three quantities α_0^{100}, α_{100}^{357}, and α_0^{357} have a similarly simple approximate relation to each other; for

$$\frac{s'-s}{t'-t}=s_0\alpha_0^{100} \qquad \frac{s''-s'}{t''-t'}=s_0\alpha_{100}^{357} \qquad \frac{s''-s}{t''-t}=s_0\alpha_0^{357}$$

whence

$$\alpha_0^{100}(t'-t)+\alpha_{100}^{357}(t''-t')=\alpha_0^{357}(t''-t)$$

whence, furthermore, for instance,

$$\alpha_0^{100}-\alpha_0^{357}=\frac{t''-t'}{t''-t}(\alpha_0^{100}-\alpha_{100}^{357})$$

and since $(t''-t')/(t''-t)$ is a constant these reductions are also mental.

It has been observed that the corrections throughout affect only a few units of the last figure, and it is for this reason that the reductions are simple. As a matter of corroboration α for Nos. 0, 1, 2, 3 was calculated directly by the quadratic formula. The results were:

No. 0...... $\alpha=0.002328$
1.... .$\alpha=0.001827$
2...... $\alpha=0.001492$
3.... ..$\alpha=0.001323$

which agree substantially with the other values in Table 34.

The values of $f(0)$ and $f'(0):f(o)$ being thus carefully revised it will be expedient to follow the suggestion to which I adverted a moment ago, and put

$$f(0)\,(f'(0):f(0)+m)=n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By constructing the revised data in Table 34 and taking their graphic mean locus I derive the following pairs of correlative values:

$x=12$ $\quad y=0.00295$
$x'=25$ $\quad y'=0.00130$
$x''=50$ $\quad y''=0.00054$

from which, deducing the constants m and n,

$$m=0.000226 \qquad n=0.0381$$

and the locus $f(0)\,(f'(0):f(0)+m)=n$ does not differ appreciably from the mean locus graphically selected.

Having thus satisfactorily made this preliminary survey it is finally desirable to calculate the constants m and n by the method of least squares. Before doing this equation (5) may be put under a better form for practice by writing

$$f'(0):f(0)=\frac{n}{f(0)}-m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $\frac{1}{f(0)}$ is simply the zero value of electrical conductivity of the alloy whose temperature-coefficient is $f'(0):f(0)$. Equation (6), when operated on by the method of least squares, does not give inordinate preference to the values $f(0)$ of high resistance, and since the high values can not be warranted with a greater degree of accuracy than the low values, equation (6) may most expediently be made the basis of computation. This I have done, and the results in Table 40 contain the observed values of $f(0)$ and $f'(0):f(0)$, the calculated values $f'(0):f(0)$, and the errors, and finally the constants m and n, with the probable errors $\Delta_\pi(m)$ and $\Delta_\pi(n)$ of each, supposing

$$\Delta_\pi(m)=0.674\sqrt{\frac{\Sigma(\Delta y)^2}{k-2}\;\frac{\Sigma\frac{1}{x^2}}{k\Sigma\frac{1}{x^2}-\left(\Sigma\frac{1}{x}\right)^2}}$$

$$\Delta_\pi(n)=\sqrt{\frac{\Sigma(\Delta y)^2}{k-2}\;\frac{k}{k\Sigma\frac{1}{x^2}-\left(\Sigma\frac{1}{x}\right)^2}}$$

where k is the number of observations and the factor $\left(1\pm\frac{0.5}{\sqrt{k}}\right)$ has been suppressed, and where x and y stand, respectively, for $f(0)$ and $f'(0):f(0)$. The last three alloys, 10, 11, 12, were added subsequently to the calculation.

TABLE 40.—*Computation of m and n in equation* (6).

No.	$f(0)$	Observed. $f'(0):f(0)\times 10^3$	Calculated. $f'(0):f(0)\times 10^3$	Error. $\times 10^3$	Alloy.
0	14.91	2.33	2.34	−0.01	Pt
1	18.53	1.84	1.84	−0.01	Au
2	22.13	1.49	1.51	−0.02	Au
3	24.67	1.33	1.34	−0.01	Au
4	19.06	1.87	1.79	+0.08	Ag
7	19.42	1.76	1.75	+0.01	Pd
8	20.40	1.67	1.66	+0.01	Pd
9	23.64	1.30	1.40	−0.10	Pd
13	31.75	0.91	1.00	−0.09	Cu
14	33.59	0.83	0.93	−0.10	Cu
15	63.56	0.21	0.40	−0.19	Cu
48	25.29	1.31	1.30	+0.01	Cu
49	53.60	0.34	0.51	−0.17	Cu
16	21.67	1.75	1.55	+0.20	Ni
17	26.84	1.39	1.21	+0.18	Ni
18	32.76	1.11	0.96	+0.15	Ni
19	28.56	1.11	1.13	−0.02	Co
20	39.62	0.93	0.76	+0.17	Co
41	23.97	1.43	1.38	+0.05	Co
22	36.33	0.74	0.84	−0.10	Fe
23	41.80	0.67	0.71	−0.04	Fe
24	59.92	0.37	0.44	−0.07	Fe
42	62.52	0.46	0.41	+0.05	Fe
43	28.75	1.21	1.12	+0.09	Fe
50	60.16	0.46	0.43	+0.03	Steel
51	40.16	0.81	0.58	+0.23	Steel
25	27.37	1.17	1.19	−0.02	Cr
26	40.87	0.66	0.73	−0.07	Cr
27	52.35	0.58	0.52	+0.06	Cr
44	31.09	0.98	1.02	−0.04	Cr
28	21.52	1.57	1.56	+0.01	Sn
29	25.60	1.29	1.28	+0.01	Sn
30	39.86	0.70	0.75	−0.05	Sn
32	21.18	1.58	1.59	−0.01	Al
33	25.64	1.33	1.28	+0.05	Mn
34	48.87	0.55	0.58	−0.03	Mn
35	15.96	2.20	2.18	+0.02	Mo
36	18.95	1.78	1.80	−0.02	Mo
45	16.40	2.12	2.11	+0.01	Mo
37	14.64	2.30	2.38	−0.08	Pb
46	17.00	2.09	2.03	+0.06	Pb
38	29.48	1.12	1.09	+0.03	Sb
47	15.83	2.12	2.19	−0.07	Bi
52	44.19	0.57	0.66	−0.09	Zn
54	24.51	1.41	1.35	+0.06	Zn
A	12.04	2.96	2.94	+0.02	Pt
C	13.27	2.50	2.66	−0.16	Pt
10	19.42	1.76	1.75	+0.01	Ir
11	20.40	1.67	1.66	+0.01	Ir
12	23.64	1.30	1.40	−0.10	Ir

The constants to which the values of this table refer are

$$m=0.0001939\pm 0.0000233 \qquad n=0.03778\pm 0.00054$$

The probable errors of m and n indicate that the inaccuracy is largely incurred in the measurement of $f'(0):f(0)$, whereas n is much more fully warranted. The equation is one, however, in which pairs of values of m and n, either both larger or both smaller than the critical values above, readily compensate each other. As usual, the constants which may be derived with a little forethought from careful graphic representations of results are probably nearer the truth than the values which are mechanically computed by the method of least squares.

The final results of this chapter may therefore be stated as follows:

In endeavoring to describe the platinum alloys as a class possessing generic characteristics, it is permissible to abstract from the minute and individual behavior of the isolated alloy; and it appears that electrical temperature-coefficient $f'(0):f(0)$ varies as a linear function of conductivity $(1:f(0))$ throughout the whole enormous variation of resistance (10 to 65 microhms, c. c.) which platinum alloys not too highly alloyed (<10 per cent.) present. In other words, if at t^0 the specific resistance of a platinum alloy be denoted by $f(t)$, where t symbolizes temperature, then

$$f(0)\,(f'(0):f(0)+0.000194)=0.0378 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is perhaps not superfluous to remark in passing that if instead of the thoroughly arbitrary temperature 0° centigrade some other value more in keeping with the qualities of platinum alloys had been selected the constants m and n would present different values; and it is easily conceivable that correlated values of $f(t)$ and $f'(t)$ may exist, for which the constant m is annulled and for which equation (7) takes its simplest form. The actual search for such a result involves more labor than I can at present apply. Clausius[1] was the first to call attention to the approximate proportionality of the resistance of most pure metals with their absolute temperature.

Accepting Matthiessen's general relation

$$s_t=s_0(1+\alpha t-\beta t^2) \qquad \alpha=0.00382 \qquad \beta=0.00000126$$

and putting

$$\frac{ds_t}{dt}=\frac{s_0}{273},$$

it appears that at, say, 60° the said proportionality is accurate. Again, since $f(t)$ increases more rapidly than $f'(t)$ decreases, with increasing temperature the passage of the equation

$$f(0)\,(f'(0):f(0)+m)=n \text{ into } f(t)\,f'(t):f(0)=n',$$

may be looked for in the region of positive t.

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[1] Clausius: Pogg. Ann., 4th series, vol. 14, 1858, p. 650; cf. Bull. U. S. Geol. Survey, No. 14, 1885, p. 24.

Other relevant results.—A research into the relations of electrical conductivity and temperature makes up an important part of the labors of Matthiessen. In addition to his well-known results for pure metals, Matthiessen[1] and his friends investigate the electrics of alloys Pb, Sn Au, SnCu, SnAg, ZnCu, AuCu, AuAg, PtAg, PdAg, CuAg, FeAu, FeCu, PCu, AsCu, and some other metals. Unfortunately, not all of these alloys are available for the present discussion, for Matthiessen's purpose seems rather to have been the exploitation of a great number of series or groups of alloys. On the other hand, it is my purpose to examine the electrical behavior of as many alloys as possible of a single given group. In Matthiessen's work the three PbAg alloys and the two SnAg alloys lie too far apart.

On perusing Matthiessen's and Vogt's results it appears that Pb alloys,[2] Sn alloys, and Fe alloys will have to be excluded from the present consideration, inasmuch as the data are either insufficient in number or lie too far apart from each other and from the extremes of the series, or because of mechanical difficulties encountered in making the alloys and shaping the wires. Perhaps there are other reasons. There remain a very full series of copper alloys, namely, CuSn, CuZn, CuFe, CuP, CuAs, a series of silver alloys, viz, AgAu, AgPt, AgPd, AgCu; and a few gold alloys, viz, AuCu, AuAg.

In view of the importance of these data I have computed the following tabular statement of Matthiessen's results, re-arranging the data in a way which, for my special purposes, is expedient; and I have also added Matthiessen's[3] results for pure metals. In Table 40*a* λ'_0 denotes the conductivity in Matthiessen's standards (Ag=100), α the temperature-coefficient of the alloy of which the composition is given on the same horizontal row. I have rounded off Matthiessen's large numbers, because the arbitrary errors introduced during the mechanical preparation of the alloys, together with the errors of structure and hardness and the more serious errors of imperfect homogeneity make the extreme accuracy of the electrical datum illusory. The table furthermore contains λ_0, the electrical conductivity in microhms referred to the cubic centimeter. This reduction is made by means of mercury.[4] In the last two columns of Table 40*a* the value of α, computed by the formula $\alpha+m=n\lambda_0$ and the corresponding errors are inserted. Of these reresults further mention will be made below, and I need here state only that the constants m and n, given at the end of the table, were derived from all the observations by the method of least squares. The com-

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[1] Matthiessen and Vogt: Pogg. Ann., vol. 12, 1864, p. 19.

[2] The metallic ingredient present in the alloy in larger amount is fitly used in designating the alloy.

[3] Matthiessen u. v. Bose: Pogg. Ann., vol. 115, 1862, p. 353.

[4] Jenkin, who made similar reductions in the case of pure metals by means of lead, arrives at somewhat different numbers. A satisfactory absolute table can not be constructed.

positions given are volume percents, except in the case of phosphides and arsenides of copper, where mass percents are meant.

TABLE 40a.—*Showing Matthiessen's and Vogt's results for the electrics of gold, of silver, and of copper alloys.*

	Alloy.	Composition.	λ'_0	Observed.	Microhms.	Calculated.	
				$a \times 10^3$	$\lambda_0 \times 10^3$	$a \times 10^3$	$\delta a \times 10^5$
Gold alloys	Au	....	79	3.67	506	3.69	−2
	AuCu	1.6 % Cu	56.1	2.65	359	2.63	+2
	AuCu	18.3 % Cu	16.1	* 0.75	103	0.79	−4
	AuAg	20.1 % Ag	21.5	1.11	137	1.03	+8
	AuAg	47.9 % Ag	15.1	0.70	9	0.74	−4
Silver alloys	Ag	....	109	3.82	691	3.83	±0
	*AgCu	1.5 % Cu	79.7	(?)4.12	510	....	....
	AgCu	8.2 % Cu	80.3	2.75	514	2.88	−13
	AgCu	46.7 % Cu	74.9	2.80	480	2.69	+11
	AgPt	2.5 % Pt	31.6	1.24	202	1.20	+ 4
	AgPt	5.0 % Pt	18.0	0.77	115	0.73	+ 4
	AgPt	9.7 % Pt	6.7	0.33	43	0.34	− 1
	AgPd	23.3 % Pd	8.5	0.32	55	0.41	− 9
	AgAu	19.9 % Au	21.7	0.90	139	0.86	+ 4
Copper alloys	Cu	....	102	3.87	653	3.98	−11
	CuAg	1.6 % Ag	89.5	3.45	573	3.54	− 9
	CuAg	4.8 % Ag	82.3	3.25	527	3.29	− 4
	CuAg	22.4 % Ag	69.8	3.03	447	2.85	+18
	CuAu	0.7 % Au	84.0	3.32	538	3.35	− 3
	CuAu	19.2 % Au	20.5	0.86	131	1.11	−25
	CuFe	0.5 % Fe	38.9	1.55	249	1.76	−21
	CuZn	5.0 % Zn	60.4	2.47	....	2.52	− 5
	CuZn	10.9 % Zn	46.9	2.05	300	2.04	+ 1
	CuZn	23.6 % Zn	21.3	1.88	136	1.14	+74
	CuZn	29.4 % Zn	21.7	1.27	139	1.15	+12
	CuZn	42.1 % Zn	21.8	1.37	140	1.16	+21
	CuSn	1.4 % Sn	62.5	2.68	....	2.59	+ 9
	CuSn	6.0 % Sn	19.7	1.00	126	1.08	− 8
	CuSn	11.6 % Sn	12.1	4.69	77	0.89	−12
	CuSn	12.3 % Sn	10.2	0.67	65	0.74	− 7
	CuSn	14.9 % Sn	8.8	0.55	56	0.69	−14
	CuP	1.0 % P	23.6	1.32	151	1.22	+10
	CuP	2.5 % P	7.3	0.48	47	0.64	−16
	CuAs	Trace	61.1	2.64	391	2.54	+10
	CuAs	2.8 % As	12.9	0.74	82	0.84	−10
	CuAs	5.4 % As	6.3	0.51	40	0.61	− 9

$$a + m = n\lambda_0$$

Gold alloys: $m = -0.000045 \pm 0.000030$
$n = +0.00721 \pm 0.00010$

Silver alloys: $m = -0.000112 \pm 0.000031$
$n = +0.00538 \pm 0.00085$

Copper alloys: $m = -0.000386 \pm 0.000040$
$n = +0.000551 \pm 0.00012$

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* Rejected.

In interpreting these results graphically it is necessary to proceed with caution; for inasmuch as specific resistance enters into them reciprocally, large values of resistance will be only inadequately represented. The tables contain many such values, nevertheless, enough data remain to exhibit the striking linear character of the curves on which the gold, silver, and copper points, respectively, lie. It is certain that the initial tangent coincides with the initial curves throughout an enormous extent of their course. Matthiessen,[1] who expressed this result under a somewhat involved form, was well justified in computing by means of it the conductivity of a pure metal from data found for metals slightly impure. This computation premises the truth of Matthiessen's other principle that, with certain distinct exceptions, the electrical temperature-coefficients of all pure metals are the same.

After Matthiessen and Vogt the curious relation in question seems to have failed to enlist further attention. It will be desirable therefore to endeavor to add to these results of Matthiessen and Vogt[2] and of myself, and to make a test of the corresponding properties of a group of metals whose electrical relations to temperature differ very largely from those relations which hold for platinum, silver, gold, copper, zinc, cadmium, tin, lead, arsenic, antimony, bismuth. I refer to the group of iron metals (iron, nickel, cobalt), more especially to the iron-carburets.[2] The latter also present an unusually large range of electrical variation; and the fairly complete set of results investigated by Dr. Strouhal[3] and myself is available for discussion. If to these be added Matthiessen's result for pure iron, and a mean curve be passed through all the observations graphically, the following principal co-ordinates of this curve,

$x=15$,	45,	70,
$y=0.00420$,	0.00166,	0.00130,

if interpreted by the equation $(x+l)(y+m)=n$, lead to the constants,

$$l=-3.73, \qquad m=-0.000706, \qquad n=0.0394.$$

These constants do not reproduce the graphic curve satisfactorily, neither has the constant l here the negligibly small value found for it in working with platinum alloys. In view of these results, it is desirable to exclude the interpolated value for pure iron, and to use only our own values for steel and cast-iron. It is not possible to reduce Matthiessen's value to our own satisfactorily, and the small datum for pure iron (large reciprocal) has an undue influence in modifying the constants to be obtained by the method of least squares. If cast-iron be also withdrawn the results for steel form a unique series, the data being obtainable by

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[1] Matthiessen and Vogt: Philos. Mag., London, 4th series, vol. 27, 1863, p. 467; Pogg. Ann., vol. 122, 1864, p. 19.

[2] This is particularly desirable here, because Matthiessen's and Vogt's iron alloys do not seem to conform to the principle here in question,

[3] Bull. U. S. Geol. Survey, No. 14, 1885, p. 15.

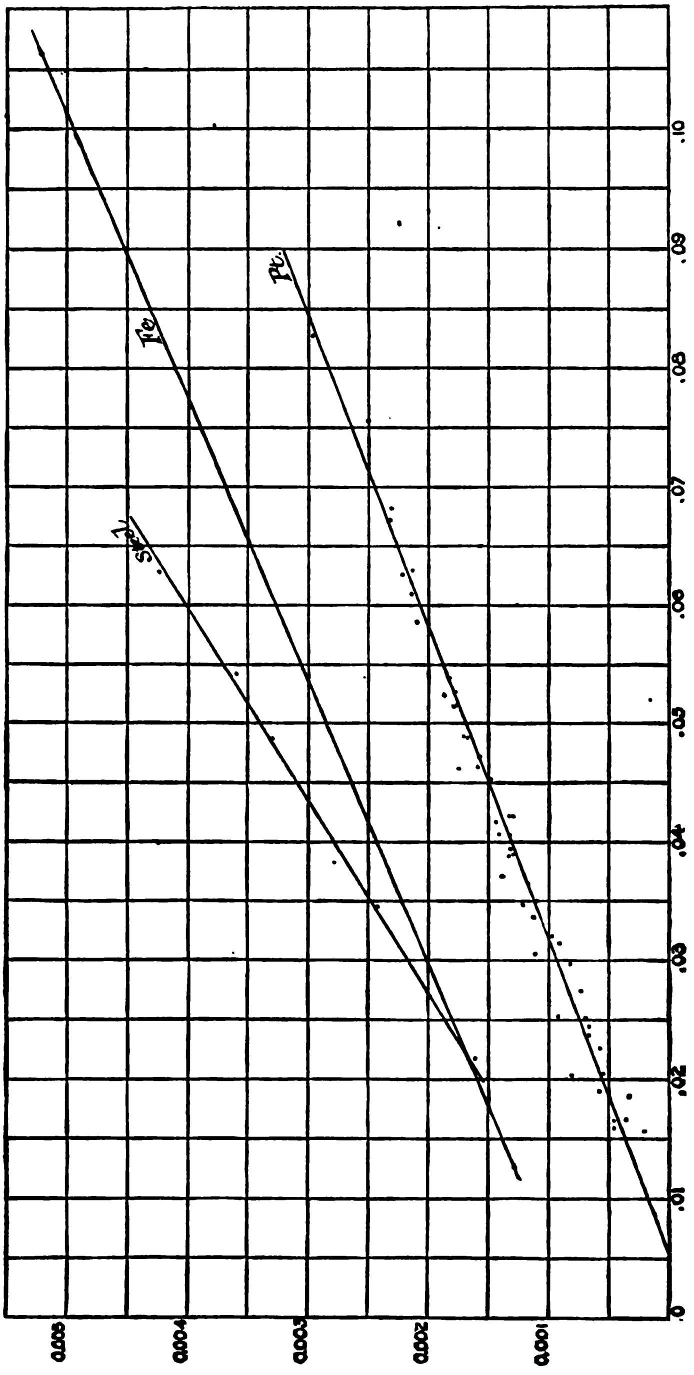

FIG. 27. Chart showing the relation between electrical conductivity and temperature of platinum and other alloys.

panied by a modification of molecular structure. The passage from the molecular type, which characterizes the first metal in the pure state, to the type which characterizes the second pure metal in the alloy is undoubtedly so complex that it is only on approaching very near the pure metals that the nature of the elementary principles of such a passage can be discerned. This is the interpretation which I venture to give to the linear loci investigated. Perhaps the following comment will make my meaning clearer:

The temperature-coefficients for pure metals are nearly constant and independent of the resistances of the metals themselves, whereas their specific resistances vary enormously. Hence the locus (Fig. 27), if extended for higher percents, must show very decided curvature. Moreover, there will be a special locus for each metal alloyed to platinum, which will terminate in the particular co-ordinates $f(0), f'(0) : f(0)$ of the metal in question. It is in the neighborhood of the two pairs of $f(0), f'(0) : f(0)$, which (one pair at each end) terminate the locus expressing the general relation between these two quantities, that the curious linear relation in question seems to hold.

In view of the fact that the relation between $f(0)$ and $f'(0) : f(0)$ must ultimately be curvilinear, the inferences to be derived from equation 6 by making either $f(0)=0$ or $f'(0) : f(0)=0$ are necessarily involved. To interpret it, similar relations would first have to be developed for low percentage alloys of many other metals. Nevertheless, these considerations are suggestive. They point to a limit, below which neither the electrical conductivity of metals nor the temperature-coefficient can be reduced. It appears therefore that a lower limit, both of conductivity and of temperature-coefficient, is among the conditions of metallic conduction, not to say of metallic state.

To make what I have here in mind clearer I will premise the following: In the case of conduction of electricity in metals (solid or liquid) the effect of temperature is a decided decrease of conductivity, continuing so long as temperature increases. In the case of conduction in non-metals or in electrolytes (solid or liquid), on the other hand, the effect of temperature is a decided increase of resistance, which, supposing the liquid state to be retained, continues as temperature increases. Hence conduction in metals is distinguished from conduction in electrolytes in this respect, that if the temperature-coefficient in one case (metals) be regarded positive its value in the other case (electrolytes) will necessarily be negative. Applying these general principles to the above inferences for alloys, it appears that the occurrence of a lower limit of electrical conductivity and of temperature-coefficient in the case of alloys may be regarded as significant or as being a unique expression of one of the conditions of metallic conduction.

I am thus led to inquire into the nature of that class of substances whose temperature-coefficient is zero; a class of substances, in other words, in which the metallic and the electrolytic modes of electric conductivity may be supposed to converge, for a march from the extremes of high values of conductivity possessed by metals or by substances of positive temperature-coefficients to the extremes of low values of conductivity possessed by electrolytes or by substances of negative temperature-coefficients can hardly be supposed possible with the exclusion of the zero temperature-coefficient.

The point which I am endeavoring to make becomes even of greater importance if we associate with metallic conductivity the correlative property of optic opacity. Relations between light and electricity have long been investigated, and many curious experimental facts are known. Maxwell's electro-magnetic theory of light furnishes a theoretical basis for the fact that all true conductors must be exceedingly opaque. Looking for a special application of this general principle it appears that solid metals, no matter how high the temperature to which they are heated, retain positive values for the temperature-coefficient. Similarly, Govi's[1] careful experiments prove beyond a doubt that solid metals, even in extreme states of red heat, remain opaque. The case of liquid metals is by no means so definitely established; and however uncertain and indefinite the evidence, the questions relative to possible transparency of liquid metals at very high temperatures is an open one.[2] Considered from an electrical point of view, the increase of resistance of a metal from low temperature to the highest attainable, accompanied, as it is, by a diminution of the temperature-coefficient, points more emphatically to an ultimate occurrence of optical transparency after the metal has passed from the solid into the fused state. Finally, inasmuch as optical transparency may be considered as having been reached at the critical temperature, it is to this state that the occurrence of the zero temperature-coefficient is to be referred.

For the present I may state that the position to be taken with reference to the importance of this paragraph depends solely upon whether or not the result underlying Figs. 26 and 27 is to be taken as the expression of a law. I have ventured to accept it as such. The remainder of the text is an application of simple geometric methods. I am not conscious of having forced any point, and the equation between $f(0)$ and $f'(0) : f(0)$, at which I finally arrive (page 157), follows as an immediate inference. If in this equation either the first or second of these quantities be made zero, or if, in other words, the line be prolonged in a negative direction, the predictions of the line as a whole agree with the known electric behavior of metallic conductors, and with the known electrical behavior of electrolytic conductors, and furthermore suggest the possible occurrence of an intermediate class of conductors, such that the passage from metallic to electrolytic conduction may be made continuously.

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[1] Govi: C. R., vol. 85, 1877, p. 699; Secchi: Ibid., vol. 64, 1867, p. 778.

[2] W. Ramsay: Chem. News, vol. 55, 1887, pp. 104, 175; Turner: Ibid., p. 163.

CHAPTER IV.

THE CALIBRATION OF ELECTRICAL PYROMETERS BY DIRECT COMPARISON WITH THE AIR THERMOMETER.

DISPLACEMENT METHODS OF AIR THERMOMETRY.

Some time after the methods for measuring high temperatures and of measuring vapor densities at high temperatures had been fully developed in the admirable manner due to Deville and Troost,[1] a new method for high temperature vapor densities was published by V. Meyer. A modification was at once introduced by Crafts and Meier, by which V. Meyer's method became available for the measurement of high temperatures. In these thermometers the gas used, instead of being kept at constant pressure or at constant volume, as in most air thermometers, or instead of being pumped out by a mercury air-pump, as in Deville and Troost's apparatus, is simply chased out by a second gas. If therefore the two gases be collected over a liquid in which the displacing gas only is soluble, the volume of the gas which fills the thermometer at any temperature is easily measurable. Air, for instance, may be used for measurement, expelled by HCl or CO_2, and collected over water. A few minutes suffice for the displacement. Since all operations are conducted under atmospheric pressure, it is obvious that the Crafts and Meier devices can be used at temperature at which porcelain is seriously viscous and permeable to gas.

Special forms of the Crafts and Meier apparatus are made by MM. Morlent frères, among which the tubular form designed by Meyer[2] to fit the Fletcher organic combustion furnace would appear to be specially convenient for calibration work. In some earlier experiments Dr. Hallock and I endeavored to make use of it. The accompanying diagram, Fig. 28, drawn to the scale $\frac{1}{10}$, indicates the method of adjusting the thermometer for calibration.

The tubular thermometer of porcelain is shown at *A B C*. The ends *A* and *C* of both of the capillary tubes *A F* and *E C* are provided with three-way cocks of special construction, made of brass. Only one of these, *D*, is shown in the diagram, Fig. 28 being a longitudinal section with an end view cross-section through the canals. The thermo-element to be compared with the air thermometer is stretched along its axis with the hot junction at *a*, the center of figure. The two wires *a b* and *a c* pass through the capillary tubes *A F* and *E C* and through a corresponding

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[1] Cf. Introduction, p. 27 et seq., where the full references are given.

[2] V. Meyer: Chem. Ber., vol. 15, 1882, p. 1161.

straight capillary canal in the stop-cocks. To prevent escape of air at these holes the wires are, during the measurements, sealed into them with resinous or other cement.

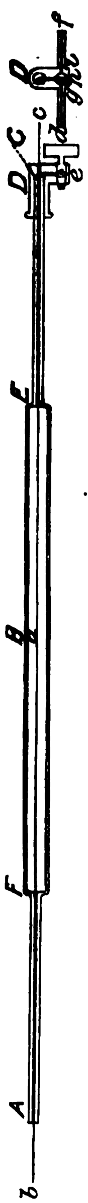

FIG. 28. Tubular displacement air thermometer. Scale $\frac{1}{8}$.

The capillary stem of the air thermometer communicates, however, with a second capillary canal in the stop-cock *D*, at right angles with the other canal. It is through this second canal and the three-way cock that either the soluble or the insoluble gas may be introduced into the thermometer, the two lateral tubes *d g* and *f t* being in connection with the corresponding gasometers. There is also a hole at *n*, through which either gasometer may communicate with the atmosphere.

We did not carry this method of calibration into great detail, chiefly because the temperature at any given point of the long tubular space of the Fletcher furnace, as well as the mean temperature of the whole length of tube, proved to be insufficiently constant. Nor can it be assumed that the temperature at the center *a* of Fig. 28 (thermo-element) is identical with the mean temperature of the tubular column of gas. Moreover, since the capacity of the thermometers is not much over 100^{cc}, measurements of gas volume must be made with very great care to be in keeping with the accuracy of calibration required. It is also inconvenient to insert a special thermo-element permanently for each series of measurements, the problem of calibration being usually of such a kind as to make it desirable to compare a series of thermo-elements either at once or else in rapid succession. Finally, the thermo-element to be compared must necessarily be filiform and very long, whereas the constants of short thick thermo-elements are frequently in demand. Add to these even more serious sources of error, inasmuch as measurements are made in a tube not glazed internally and with a gas, the rigorous purity of which is not assured. Nevertheless this method of calibration may sometimes be convenient. (Cf. p. 36.)

Taking the elaborate gasometric apparatus into account the method is not as simple as it appears. It occurred to me, however, that this simplicity might possibly be reached by displacing dry air with slightly superheated steam. But I made no experiments.

The application of Crafts's method, which can easily be made by inserting a platinum capillary tube into the stem of the air thermometer, deserves special notice, and by the aid of the metallic tubing, to be described below (Chap. V), can be put to a rigorous test.

CONSTANT-VOLUME THERMOMETERS.

In most of the present experiments the object has not been to test the rigorous accuracy of the air thermometer so much as to devise forms of apparatus in which such tests can be satisfactorily made. I have had in mind, moreover, that the thermometer is to be used as a means of calibrating the thermo-element. Having found therefore that at temperatures not exceeding 1,300° the porcelain of Bayeux is quite rigid as regards excesses of pressure (internal or external) not exceeding one atmosphere, I made the early air-thermometer measurements by the constant-volume method. Jolly's[1] well-known and convenient manometer was largely used, with such modifications as the special work required. To connect bulb and manometer of the air-thermometer adjustment I used capillary metallic tubes. Such tubes had been used by Regnault[2] and others before. They enable the observer to place the manometric apparatus at some distance from the furnace and the bulb, a condition of accurate measurement which, at high temperatures, is almost essential. I will briefly describe the apparatus more in detail. The general disposition of apparatus is given in Fig. 29 (frontispiece), and there will be little difficulty in recognizing the parts to which the descriptions refer. Further comment is made below (p. 188).

Manometer.—A very substantial form of manometer stand, made for the work by Mr. William Grunow, of West Point, is shown in the frontispiece, under B. The stand is essentially that of Jolly, as modified by Professor Pfaundler in Insbruck.[3] It consists of two vertical parallel cylindrical slides made of brass, 160^{cm} in length, 2.5^{cm} in diameter, and about 13^{cm} apart, measuring from center to center. These slides (tubular) are fastened below to a suitably large tripod support, and are braced above by a slender St. Anthony's cross, the lower end of which abuts against the tripod. Metallic clamps or sleeves, provided with suitable devices for carrying the manometer tubes, are thus free to slide along the whole vertical range of 160^{cm}. A millimeter scale, about two meters long, is placed between the brass upright for approximate measurement. Finer measurements are made with a cathetometer.[4] Obviously this stand is equally convenient as a support for both the constant volume and the constant pressure apparatus, either of which methods of air thermometry may be used with equal facility. The modification of the Jolly-Pfaundler stand, by which the brace is made to abut against the top of the slides instead of against the middle, as in the old form, is due to Dr. Hallock. I have modified the Jolly-Pfaundler stand by using four parallel slides of about the length and distance apart of those just described (Fig. 43). The two front slides are used for the manometer

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[1] Jolly: Poggendorff Annalen, Jubelband, 1874, p. 82.

[2] Regnault: Relation des expériences, Paris, 1847, p. 264.

[3] Cf. Müller Pouillet, Physik, vol. 2, 1879, p. 119.

[4] Mr. Grunow's form.

proper; the two rear slides for the "compensator" manometer for adjustable screens, etc. The four uprights, firmly screwed to a base below and to a cap plate above, possess all the stability desirable, without any braces at all. The cap piece carries threaded holes, into which vertical or horizontal rods can be screwed, to give further length or height to the apparatus whenever necessary. In figure 43 this form of stand is used to support the pneumatic apparatus in the viscosity measurements.

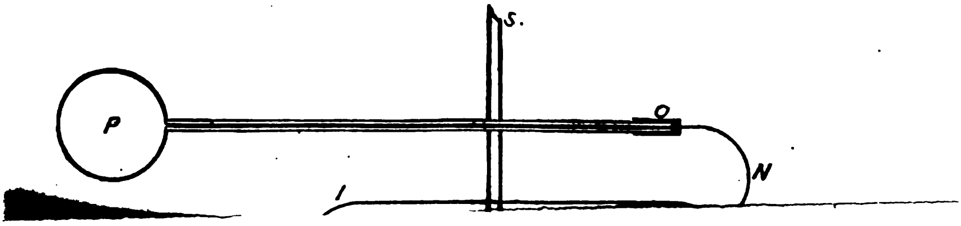
Fig. 30 gives a more succinct account of the method of adjusting the parts of the air thermometer, the parts being drawn about one-sixth of actual size.

The manometer proper, *A B C D E F G*, has the usual terminal glass tube *A B* about 2^{cm} or more internal diameter, which is joined to a length of about 2 meters of rubber hose, doubly wrapped by a steel three-way stop-cock, *B*. This carries a lateral tubulure, through which superfluous mercury in the tube *A B* may be tapped off, an operation often desirable when the constant-pressure method is used, in which case the tube *A B* may be expediently chosen wider. *B* may also be shut off to keep the mercury column at a fixed height. The metallic sleeve of the manometer stand, which clutches the tube just below the faucet *B*, is provided with a micrometer screw (thread 0.1^{cm} apart) by which the height of the meniscus may be adjusted with nicety.

The other end, *H*, of the rubber tubing is joined to the lateral branch of this glass barometer tube *H E F G*, held by the second slide of the stand. This widens above between *F* and *G* to allow freer play of the upper meniscus. Inasmuch as it is frequently necessary to employ air thermometers, glazed on the outside only, it is desirable to work so far as possible with pressures less than an atmosphere. The result is a tendency to force the viscous glaze into the pores of the porcelain. Satisfactory work with low pressures is possible only when the upright branch *E F* is impervious to air. Hence it is made of glass, like an ordinary barometer tube, and all rubber connections and tubing here are discarded. It is convenient, however, to insert a glass stop-cock at *F*, (Fig. 30), but not essential. A stop-cock is always an opportunity for leakage.

The top *G* of the tube *E G* may either be drawn to a fine aperture, just large enough to admit the end of the capillary platinum tube *G I K M N O*, or it may be cut off straight and admit a rubber stopper sealed in with resinous cement, through which stopper the platinum tube passes. In either case this end of the platinum tube, sharpened to a needle-like point below the mouth of the capillary canal, subserves the purpose of a fiducial mark excellently. In the constant-volume method the volume of the space above the meniscus must be small and accurately known. Hence it should be nearly cylindrical in figure, and the part *F G* of the barometer tube not chosen too wide.

The extreme end of the capillary tube passes symmetrically through a metallic cap, *O*, the top of which is soldered hermetically to the tube.


S.
P
O
N
I

The end in question projects somewhat beyond the lower edge of the cap, the inner width of which is such as to fit snugly around the stem of the porcelain air thermometer *O P*. Capillary tube and stem are fastened with resinous cement[1] in this manner: The cap is clamped vertically with the open end uppermost in a vise and filled with melted cement, kept slightly above the melting point by applying a burner. The stem of the air thermometer is then inserted from above and in such a way that the projecting capillary tube may pass into the capillary canal of the stem. The cement which exudes is not removed until the two parts have thoroughly cooled in the upright position in which they were clutched by the vise.

Metallic capillary tubes.—The capillary tube being some two meters long, it is convenient, or perhaps even essential for quick manipulation, to insert an intermediate branch stop-cock of glass, *L R*, somewhere near the middle of the tube. By connecting this cock with the exhaust pipe *R S* of a mercury air-pump, the air of the thermometer bulb may be removed in any quantity, the bulb thoroughly dried at red heat, or even filled with other gases than air, in a way which is thoroughly satisfactory. To insert the ends of the capillary tubes into the cock the following method is reliable: The inner ends of the capillary tubes are bent at right angles to their axes, and then passed through the two parallel canals of a little piece of the porcelain cylinder used above for insulating the wires of the thermo-element. The parts near the right angles are additionally secured by being tied together with fine copper wire, whereupon the whole connection (excepting, of course, the ends of the capillary canals of the metal tubes, which, for this purpose, project beyond the porcelain cylinder) is saturated with cement. The cylinder is then inserted into one tube of the glass faucet and sealed in it with cement in such a way as to leave a minimum of waste space between the cylinder and the plug of the faucet. It is well, moreover, to tie the tubes proper to a stick, so as to bridge over the severed part *L*, and thus avoid those leaks to which the joint is liable when suddenly jerked or otherwise interfered with seriously. It is convenient to make the exhaust-pipe *R S* of thin lead tubing, because this can be bent in all directions and is sufficiently rigid to maintain its figure and sufficiently impervious to gas. Two metallic capillary tubes may be coupled by pushing them in opposite directions into a short end of glass tubing, into which they fit snugly, till the ends meet near the center. Applying a drop of melted cement and the burner to the end of the glass tube, the cement is drawn into the space between the outer surface of the metallic tube and the inner surface of the glass tube by capillary attraction, so long as the cement remains liquid. This joint is excellent.

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[1] Rosin and beeswax fused together in equal parts. In soldering a wire or capillary tube axially into a large glass tube this cement must be added in thin horizontal layers, otherwise the cylinder of mastic, as it contracts on solidifying, draws itself away from the tube. Marine glue is doubtless a more reliable cement.

Heat must be cautiously applied to prevent the cement from running in far enough to stop up the capillary canals. I may add here that in later experiments I found it best to solder the ends of the capillary tubes into a little cylinder of brass, retaining in other respects the adjustment of Fig. 30. The brass cylinder is, of course, provided with two holes to receive the tubes. I have also in definite work discarded stop-cocks altogether, cementing either an open glass tube or a little closed glass cup around the brass cylinder in question, according as I wished to exhaust or to dry the air in the bulb or to make thermal measurements.

Capillary tubes may be made either of copper, of silver, or of platinum. The latter are preferable, because they do not amalgamate, and if a mercury thread is accidentally forced into them, it can be forced out again cleanly, like the thread of a thermometer. Threads accidentally injected seldom pass beyond the stop-cock *L R*, and thus the fatal accident of the injection of mercury into the thermometer bulb *P* is avoided. The capillary tubes should be seamless. I succeeded in making them of copper pretty well as follows: Taking a cylindrical copper rod 1^{cm} in diameter and in convenient lengths of 5^{cm} to 10^{cm}, central holes were drilled into them about 0.4^{cm} to 0.6^{cm} in diameter, as nearly as possible co-axial with the rod. These holes were then filled with fusible metal, and when cold the rods were rolled and drawn down to fine wire of the diameter required. The tubes were submerged carefully in boiling aniline, commencing at one end and passing to the other; this to prevent rupture in virtue of sudden expansion of the fusible core. By means of an air force-pump, or even of a high-pressure steam-boiler, acting at one end, sufficient pressure was brought to bear on the fused core to force it out completely. When this occurs bubbles issuing at the end of the tube rise in the aniline in great number. The tubes are then withdrawn from the bath, dried, and, with a current of steam passing through them, heated to redness, and tested. This process is very tedious, inasmuch as it is not always possible to so draw the tubes that the fusible metallic core remains central. When the canal is asymmetric there is liability to rupture, if it does not actually occur during the drawing.[1] For each perfect tube two or three imperfect ones must be discarded. Tubes thus made have a larger caliber relative to their thickness than is obtainable in other ways. Thin-walled capillary tubes are often specially desirable, particularly when tubes are to be soldered (with glaze) into the stem of an air thermometer. In table 41 I give the constants of copper tubes obtained by this process.

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[1] According to Rouma (cf. Spring: Chem. Ber., vol. 15, 1882, p. 595) silver with a platinum core (Wollaston's method) is found to alloy after long drawing. I observed no effects of this kind, however, possibly because the metallic surfaces, in case of base metals, are not sufficiently clean.

TABLE 41.—*Dimensions of copper capillary tubes.*

No.	Weight.	Length.	Thickness.	Caliber.	Volume per cm.
	g.	*cm.*	*cm.*	*cm.*	*cc.*
1	5.81	81.5	0.119	0.063	0.0031
2	5.39	95.0	0.103	0.050	0.0020
3	10.81	144.0	0.123	0.066	0.0034
4	4.74	67.6	0.119	0.064	0.0032
5	7.34	105.6	0.118	0.062	0.0031
6	7.07	108.2	0.119	0.069	0.0037
7	2.99	101.7	0.077	0.041	0.0013

Among these No. 7, a very perfect tube, is most remarkable. The tubes were made in February, 1884.

Since that time I was fortunate in inducing the Malvern Platinum Works to undertake the manufacture of such tubing in silver and platinum. With the latter metal they succeeded well, and the dimensions of samples of the (platinum) tubing made for me are given in Table 42.

TABLE 42.—*Dimensions of platinum capillary tubing.*

No.	Weight.	Length.	Thickness.	Caliber.	Volume per cm.
	g.	*cm.*	*cm.*	*cm.*	*cc.*
1	9.02	51.0	0.115	0.0524	0.00215
2	7.25	42.6	0.115	560	246
3	7.07	41.5	0.115	561	247
4	7.62	44.4	0.115	553	240

These tubes may be obtained in any length not exceeding 5 meters. It is usually sufficient to use meter lengths only, cleaning each thoroughly with naphtha, alkalies, and acids; passing capillary iron wire quite through the tube, drying, and then heating to redness before inserting. The use of capillary tubes presupposes slow rise and fall of temperature during calibration. To this end my furnaces have been constructed. The data of Tables 41 and 42 will appear more striking when placed in contrast with the capacities of the bulb and stem of the porcelain gas thermometer. These are 300^{cc} and 0.012^{cc} per centimeter, respectively.

Kundt has successfully used capillary glass tubes drawn out so thin as to be filamentary.

Platinum capillary tubes (the present being the first ever made, I believe) are an especially useful apparatus and subserve many ulterior purposes. They are used, in chap. V, for instance, as an essential part of the transpiration thermometer, and to investigate the laws of transpiration and gas viscosity at high temperatures.

Porcelain gas-thermometer bulbs.—Various forms of gas-thermometer bulbs, as given in Figs. 31, 32, and 33, drawn to a scale of ½, were used.

They were made by Morlent frères, Paris[1] (formerly Mr. Gosse, the original constructor of the Deville and Troost apparatus), of the very refractory porcelain of Bayeux. Fig. 31 is the earliest form. Bulb and stem are one piece, put together by the maker. The fractured bulbs show that the ballon proper, to within a radius of 1^{cm} of the neck (*d d*, Fig. 4), and the stem with attached neck (*b d a d*), were made separately, and then put together by a skilled artist. After burning no discontinuity of porcelain at the circle of junction is visible. The glazed gas-thermometer is perfectly smooth on the outside, and a longitudinal section differs in no essential respect from Fig. 31.

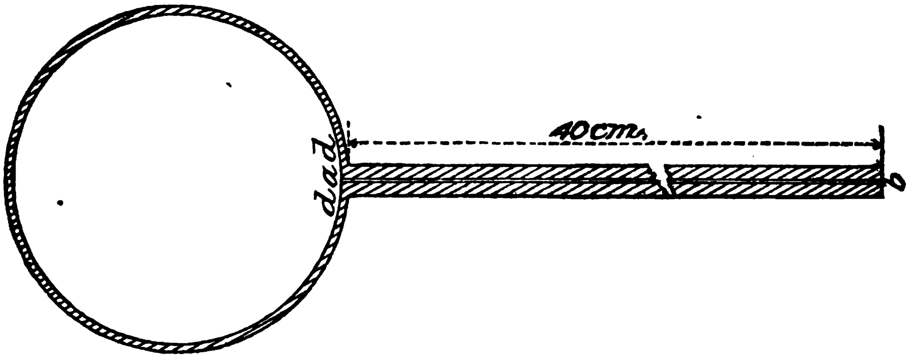

FIG. 31. Non-inglazed spherical air thermometer bulb. Scale ½.

In consequence of the long capillary stem (0.1^{cm} in diameter) it is exceedingly difficult to glaze these thermometers internally or to keep the stems from choking when the temperatures are high enough to soften the glaze. For this reason the bulbs are furnished without being glazed internally—an error when data of high temperature are to be sharply measured. I add here that on fracture the stems very frequently reveal clefts and lateral fissures communicating with the canal, I believe that a more compact stem could be made in the manner described above (p. 95) for the manufacture of porcelain insulators for the thermo-element. M. Gosse pressed his stems in a long mold over a core of zinc wire. The latter is melted and volatilized during the firing; but in spite of its ingenuity this method is imperfect, for the capillary canals made in this way, in addition to their liability to retain lateral fissures, are seldom perfectly central along the whole length of stem. In case of a stem made by my method this result necessarily follows whenever the apparatus has once been adjusted.

In Table 43 some values of the mean dimensions, etc., of the bulbs (Fig. 31) are given. They are the results of mercury or water calibrations, of which for accurate measurements the water calibrations are preferable. Mercury does not so easily enter the fine fissures.

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[1] I also had similar bulbs made in Berlin, and will communicate results obtained with them later.

TABLE 43.—*Capacity, etc., of porcelain gas-thermometer bulbs.*

No.	Bulb.			Stem.			
	Equatorial diameter.	Mean thickness of wall.	Capacity.	Length.	Thickness.	Mean caliber.	Volume per cm.
	cm.	*cm.*	*cc.*	*cm.*	*cm.*	*cm.*	*cc.*
2	9	0.27	300.0	40	0.8	0.122	0.0116
3	9	0.26	307.4	40	0.8	....	....

Probably owing to difficulties in burning the polar diameter is usually slightly less than the equatorial diameter.

To use this bulb for calibration it is necessary to have a space of very constant temperature, for the indications of the thermo-element are instantaneous, and refer only to the little space immediately surrounding the thermo-electric junction, whereas the gas thermometer passes relatively slowly from one temperature to another, and the temperature datum refers to the internal mean temperature of the whole exposed surface. These differences of character in the respective temperature indications may, of course, be seriously large. They are entirely arbitrary. With the object of eliminating these errors I had a bulb made in the shape of Fig. 32, the bottom of which is re-entrant, forming a cylindrical tube, *n m*, the closed end *m* of which projects inward as far as the center of the bulb. It is into this tube that the properly insulated thermo-element is introduced with its junction at *m*. The insulators are sufficiently large to practically close the tube *n m* as with a plug, by which loss of heat by radiation is made imperceptible. The temperature of the thermo-element and of the gas thermometer may therefore be regarded identical. I add that the stem of the form (Fig. 32) is thicker than the stem in Fig. 31, in order that at high temperatures there may be less liability to bending, supposing the thermometer to be held in a horizontal position and the stem to be slightly viscous. The widening

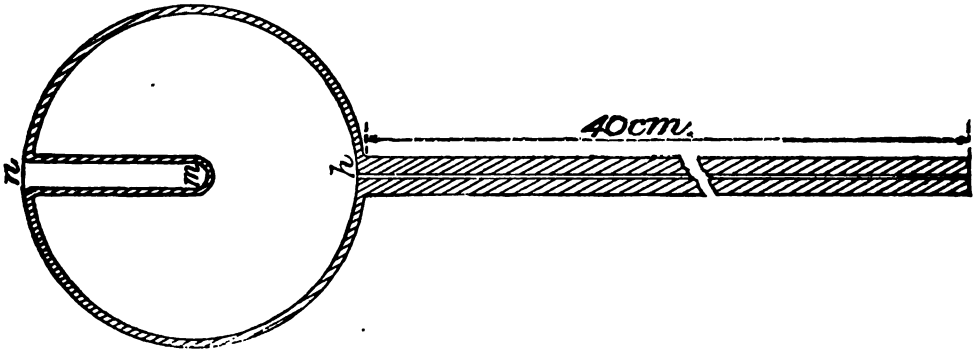


FIG. 32. Non-inglazed re-entrant air thermometer bulb. Scale ½.

of the stem does not seriously increase the value of the stem error by increasing the number of interstitial pores, as will be seen. In this re-entrant bulb symmetry of form has been sacrificed in order that greater identity in the exposure of the air thermometer and of the thermo-couple may be secured. Deville and Troost emphasize the desirability of spherical bulbs. But the expansion error is beyond question less serious than the calibration error, due to inequalities of temperature of bulb and thermo-electric junction.

The pressure which bulbs of this kind can withstand at high red heat (1,000°) without deforming appreciably is certainly greater than an atmosphere, probably much more. Bulbs in which water is confined explode at high temperature with detonation and great violence.

The results obtained with these forms of internally unglazed gas thermometers are called in question by Deville and Troost. Doubtless gas or moisture is forcibly retained in the pores of the porcelain. Hence the amount of gas in the bulb at low temperatures may be greater than the pressure datum indicates. Again, in the constant-pressure method of measurement the volume of the bulb, an essential part of the argument of the formula, can not be sharply defined. Hence the great desirability of performing the measurements with bulbs of porcelain, glazed thoroughly both within and without. Such a form is given in Fig. 33.

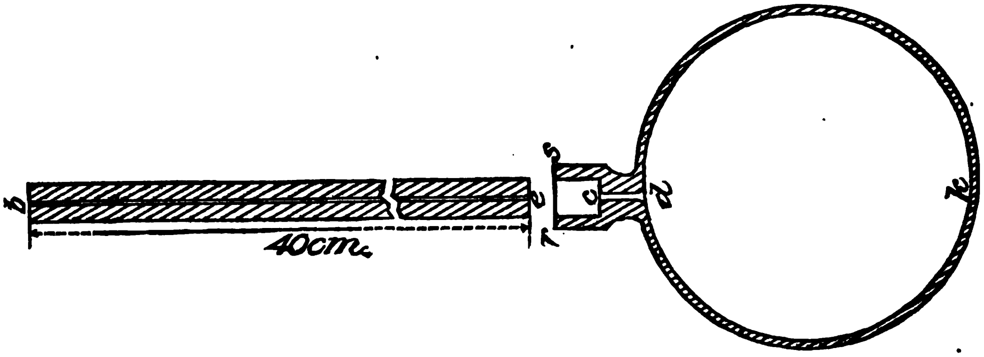


FIG. 33. Inglazed spherical air thermomoter bulb. Scale ½.

Bulb *c d k* and stem *e b* are here distinct parts. They are calibrated separately, and prior to using are soldered together with feldspar and the oxyhydrogen blow-pipe. The bulb *c d k* ends in a short neck, *c d r s*, the part *r c s* being just large enough to receive the stem *e f* snugly. The canal *c d*, through which the bulb is glazed, eventually becomes the prolongation of the capillary canal of the stem.

Soldering together the bulb and stem is a difficult operation, and calls for much skill and patience on the part of the operator. The bulbs are liable to breakage, and it is difficult so to solder the stem that the joint may be hermetically sealed. I therefore feel justified in describing a machine of my own, by which such soldering can be effected.

Machine for soldering porcelain.—The elevation (Fig. 34) is largely in section, the cuts being taken through central planes of the apparatus, as will readily be understood by consulting the plan (Fig. 35). I give the drawing in a scale of $\frac{1}{10}$. The soldering machine consists essentially of

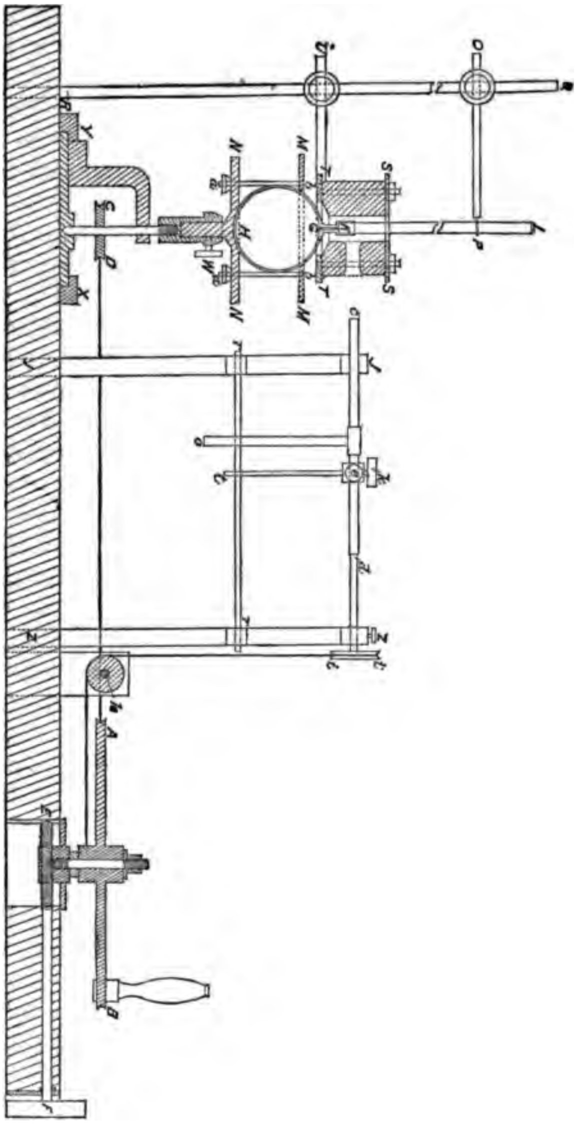


FIG. 34. Machine for soldering porcelain; elevation. Scale $\frac{1}{10}$.

a whirling-table, of which *A B* is the large pulley and *C D* the spindle. The two wheels are connected by round leather belting, which can be tightened at pleasure by a screw adjustment, *E F*. The spindle axle carries the gas thermometer bulb *H G* to be soldered to the stem *L K*. The two parallel plates of brass, *M M*, *N N*, held at any desirable distance apart by three bolts, *b a*, subserve the purpose of securing the bulb *G H* firmly and symmetrically with respect to the axis of rotation. It is easily seen that the two plates *M M* and *N N* make with the bulb *G H* a joint that is practically of the ball-and-socket kind, hence the facility of adjustment. A lateral arm, *O P*, clamped to the fixed upright rod *Q R*, holds the stem *K L* in position during the rotation, the latter passing through a little ring at *P*. Another lateral arm, *U T*, similarly clamped to the rod *Q R* carries the adjustable lime furnace. This is a rectangular parallelopipedon sawed out of a solid piece of lime, provided with a large central perforation passing quite through the block for the reception of the neck and lower stem of the gas-thermometer; provided also with a smaller lateral perforation passing only far enough to communicate with the central hole. This block of lime is secured between two parallel plates of iron by aid of three bolts, two of which only appear in the figure. The plates are, of course, ring-shaped, to correspond with the vertical perforation of the lime block, and the lower plate is riveted to the lateral arm *U T*. To obviate confusion of lines the lime furnace is omitted in the plan (Fig. 35). I need only add that the arms *O P* and *U T* can be removed at pleasure; that the bulb, with its lantern-like support, can be withdrawn from the spindle by unclamping the screw *W*; that, finally, the spindle itself is adjustable laterally at pleasure, passing, as it does, between two slides, *X X* and *Y Y*. These slides are kept in position by two pairs of screws, by which, moreover, the slides and the base plate of the spindle may be forced firmly in contact and clamped.

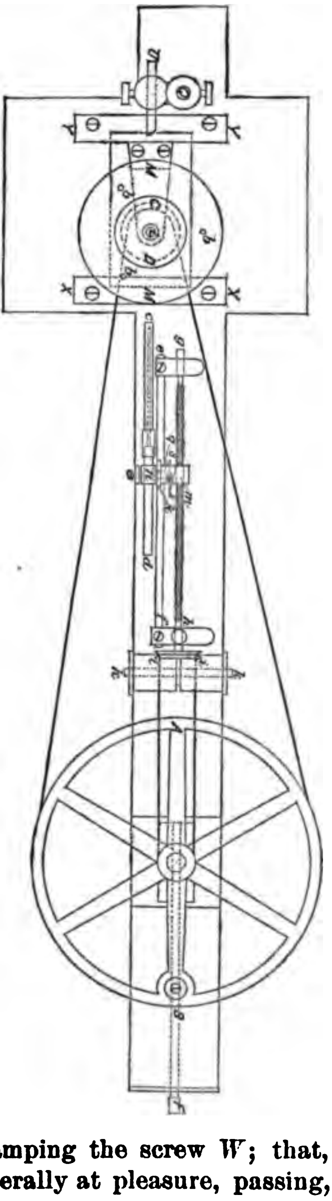


FIG. 35. Machine for soldering porcelain; plan. Scale $\frac{1}{15}$.

Having given the arrangement of the rotational apparatus, I have to add a description of the sliding oxyhydrogen blow-pipe. The blow-pipe itself is shown at *c d*, and the plan contains dotted lines showing the construction of the interior. Hydrogen from the gasometers enters through a large tubulure, *o*, fully 0.5^{cm} in diameter, compressed oxygen through a finer tubulure, *d*, the jet end of which is not quite 0.08^{cm} in diameter. This blow-pipe burns quietly, and if well constructed the flame is visibly one foot in length, tapering with perfect regularity from the large diameter 0.5^{cm} to a point. The attachment of this blow-pipe to the frame-work which carries it is such that in its horizontal position the flame plays through the lateral hole of the lime furnace, impinging upon the neck of the bulb to be soldered. The collar *n*, into which the blow-pipe is fastened by the screw *e*, has a lateral axis or swivel, in virtue of which the blow-pipe may be rotated around an axis perpendicular to itself (a kind of trunnion), and clamped at any given angle by the screw *k*. In this way the flame may be made to impinge against any part of the stem or neck of the bulb to be soldered, at pleasure. The sliding arrangement into which the swivel is clamped consists of two parts, the slide proper, *q*, moving freely along the rod *e f*, and the part *m*, which is practically a nut of the male screw *g h*. The parts *q* and *m* can be joined at pleasure by aid of the steel pin *s s* and corresponding clamp screw. If the latter be loosened the blow-pipe may be made to approach the air thermometer as near as desirable. The screw *g h* ends in a wheel, *i i*, rotated by a belt, which passes over the lower spindle of the pulley-wheel *A B*. An axle, *k k*, carries two independent rollers, by which the direction of the belt is changed. In this way the screw is kept in motion to correspond with the rotation of the air-thermometer bulb.

When the flame is lit and the soldering commenced, the blow-pipe carriage is placed as near as practicable to the end *h* of the screw. As the rotation continues the flame gradually approaches the air thermometer, and the heat is therefore intensified with perfect regularity. Inasmuch as the flame impinges on the neck while in a state of rotation, it is quite obvious that the liability to fracture or breakage is by this device diminished to a minimum. I add that to prevent interferences the thread at the end of the screw *g h* has been cut away, so that when the nut *m* is near these end points there may be no further tendency to move. An intermediate rod, *r r*, and a sliding piece, *e t*, increases the steadiness of motion. The carriage as a whole is supported by two uprights, *J J* and *Z Z*.

The feldspar to be used for soldering is to be ground most carefully to an impalpable powder and mixed with mucilage or water to a plastic or pasty consistency. This is spread uniformly around the neck of the bulb, so as to form a ring where the edge of the neck shoulders against the stem. It is then allowed to dry. Stem and neck should fit snugly from the outset; at least all waste space should be calked with feldspar, It is perhaps best to commence the heating with the lime furnace removed, sliding it above the neck. When the parts are white hot and the frothing has largely ceased, it is expedient to conduct the further soldering by hand directly, the blow-pipe being for this purpose manipulated by the right hand and the spindle turned suitably with the left. Care must be taken not to melt the porcelain. The heat is, however, sufficient to make porcelain quite viscous, and not only can the stem be bent, but the parts of the neck of the bulb surrounding the lower end of the stem may be pressed firmly against it, producing a weld joint, as it were. I have no doubt that porcelain can actually be welded in this way. Flat steel pliers, which if necessary may be notched by a cylindrical hole which fits closely around the neck, are closed quickly but firmly around the neck and then quickly withdrawn, rotation of the bulb being temporarily discontinued. The operation calls for skilled manipulation. Indeed, it is not easy to make a vacuum-proof joint, and samples neat in external appearance have frequently to be duplicated. It is essential to keep the whole neck at white heat a long time in order that its inner surface and the outer surface of the stem may be everywhere in contact. It is at this stage of the operation that the lime furnace may be appropriately lowered, and the final gradual coalescence of contiguous parts of the porcelain apparatus allowed to take place. Two oxyhydrogen flames impinging on the porcelain from opposite directions are preferable to a single flame with the lime furnace. The latter is essential, however, during cooling. Porcelain is specially liable to crack on cooling when it first becomes rigid. Hence it is expedient, after withdrawing the flame, to close up the furnace as far as possible with asbestus board and carded asbestus, and then to bury the whole furnace above the plate *mm* in a heap of slacked lime. But with the best precautions the feldspar is found to be fissured after cooling, and unless bulb and stem have thoroughly coalesced and the joint be perfect at the internal faces, the apparatus will not be vacuum-proof. It is well to fuse feldspar upon the end of the stem around the hole. To keep this hole opposite the capillary hole in the neck a thick platinum tube or wire may be thrust through both. In this case the neck of the bulb may be quite filled with the slimy feldspar paste, and the stem then forced into it from above, keeping the capillary platinum tube in place. The feldspar which exudes is partially removed, and the bulb then allowed to dry. This process gives greater assurance that soldering will take place between the inner surface of the neck and the end of the stem than any other. I may add, in closing, that I have repeatedly tried to make air thermometers in which a capillary platinum tube is soldered into the stem with a glaze more fusible than feldspar. I have also attempted to glaze single-piece air thermometers, like Fig. 31, internally, as well as to solder platinum tubes into the stem. Although these attempts have thus far failed, it is but just to assert that the failures are due rather to the insufficient technical skill of the operator than to crucial errors of method. I hope at an early day to produce a porcelain air thermometer made in one piece, glazed within and without, and provided with a tight-fitting capillary platinum stem. I also hope to make bulbs of fire-clay, suitably glazed without, apparatus which will be available for the measurement of temperature very much beyond the highest limit of the porcelain thermometer. The soldered air thermometer presupposes low-pressure measurements, such as this paper describes.

Bulbs which are not perfectly tight may sometimes be closed by heating in a large furnace with glaze. I have used the one described below for this purpose. This process, however, is difficult and expensive, even if low pressure is applied to suck the glaze into the capillary fissures and canals. It is best to endeavor to complete the soldering with the oxy-hydrogen flame, testing the quality of the joint with the air-pump after the bulb is again cold.

It is well to insert a word here about gasometers. I used the simple form of sheet zinc bell-jar *G G G G* (Fig. 35*a*), dipping in a reservoir of

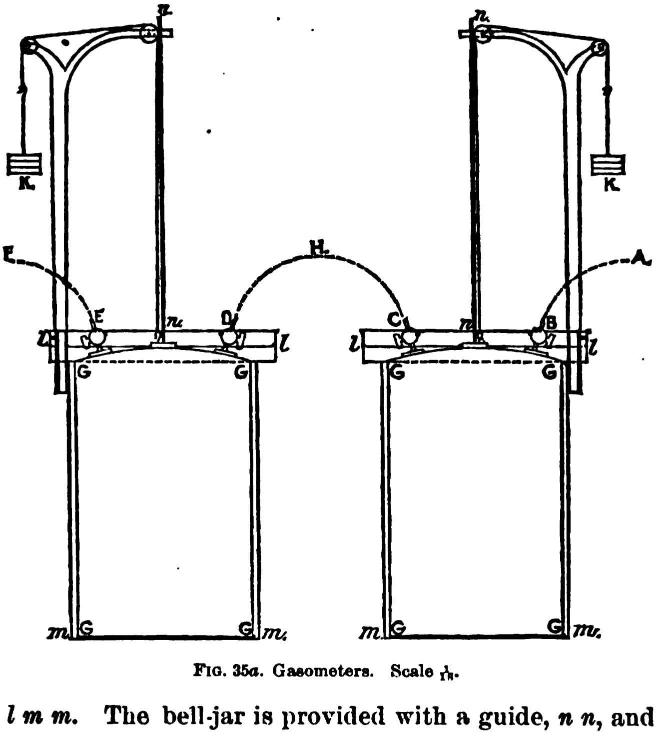


FIG. 35*a*. Gasometers. Scale $\frac{1}{15}$.

water, *l l m m*. The bell-jar is provided with a guide, *n n*, and a counterpoise, *K*. The level of the water is shown at *l l*. Gasometers of this kind are well known, and are furnished by Ritchie & Co., in Boston. My purpose in this place is to indicate the great advantage gained by two stop-cocks, *B*, *C*, for each jar, *G G*, *G G*; for in this way any number of single jars may be coupled together. In Fig. 35*a*, for instance, the stop-cock *B* is supposed to be in communication with the hydrogen generator; the stop-cocks *C* and *D* are connected by rubber tubing; the stop-cock *E*, finally, supplies the hydrogen to the blow-pipe, with which it is in communication. The advantage gained in this way is this, that the hydrogen may be generated and used at the same time—a desideratum when large quantities of the gas are necessary.

Revolving muffle.—In order that the temperature comparisons in question may be satisfactorily made, the apparatus to be compared must be placed in a space of practically constant temperature, which shall be variable at pleasure from ordinary temperatures to the most extreme degrees of white heat. Methods for securing constant temperatures for thermo-electric comparisons have already been given; but when one of the pieces of apparatus to be heated is as large as the bulb of an air thermometer, and when, moreover, this relatively large apparatus is to be compared with the sensitive point of the thermo-element, the difficulties of calibration are very much increased. In some of the earlier comparisons the efficient assay muffle-furnace made by the Buffalo Dental Manufacturing Company was used. This is practically a gigantic Bunsen burner, surmounted by a furnace of fire-clay, so constructed that the flame in a narrow sheet is compelled to pass around and completely to envelop the muffle. In the furnace used this muffle was fully 20^{cm} long and 12^{cm} high, offering ample space for the introduction of the bulb, and by wrapping asbestus paper and carded asbestus thickly around the bulb so as quite to fill the muffle, and binding muffle and thermo-element closely together, the two may be compared with some accuracy. Results of this kind are given below (p. 201.)

Unfortunately the introduction of metal envelopes is objectionable, in view of the danger of fluxing the contiguous parts of refractory clay. There are other and more serious difficulties encountered. The maximum temperature thus attainable is not greater than 1,000°, and hence the interval of calibration is limited. Moreover, the closed end of the muffle is at the center of heat of the furnace, whereas the open end is neither surrounded by flame nor are the provisions against loss of heat sufficient for constant temperature—conditions which recommend the furnace for assay purposes, but which, inasmuch as they involve differences of temperature of several hundred degrees, are seriously objectionable for calibration purposes. Again, the rate of cooling of this furnace is too great. It is difficult to close up so completely as to exclude convective cooling due to currents of air and diminish loss by radiation, the bottom of the furnace over the burner being large, open, and inaccessible, and the chimney large. Nor is it conveniently possible to regulate the flame of the burner for intensities of heat less than the maximum. Finally, thermo elements must be compared singly, because they need to be tied to the bulb. In general consecutive comparisons of series of elements are desired.

Without question the form of the furnace could be modified to meet the special requirements of the calibration problem, excepting, of course, the limited scope of temperature; but it is expedient to proceed more radically and introduce an entirely new and distinct furnace for the purposes in question. This I have done in a way indicated in plan in the diagrammatic Fig. 36. The body of the furnace is a thick cylindrical box, *B B*, surmounted by a hemispherical lid suitably perforated. In this cylindrical inclosure a spherical muffle, provided with hollow lateral arms or axles, *E* and *F*, and placed symmetrically with respect to the center of figure of the furnace, is free to rotate around the horizontal axis of the arms. If the rate of rotation be sufficient this mechanism insures constancy of temperature within the muffle around the horizontal *E F*. Two blast burners, *G* and *H*, purposely placed *tangentially* or *diagonally*, so as to be equivalent to a couple, blow a cyclone of flame into this furnace, equalizing temperature around the central vertical. Virtually therefore the muffle, regarded as a geometrical sphere, has two rotations, one about an axis, *E F*, a second around the vertical, passing through *O*. To make this apparatus theoretically perfect a third rotation around an axis passing through *O* and perpendicular to *E F* would have to be supplied. This third rotation is a mechanical impossibility, bearing always in mind that cumbersome or complicated apparatus would rather detract from the end to be attained than add to it. The two rotations can be made to suffice. In the spherical space of constant temperature thus obtained is placed the bulb of the air thermometer, with its stem projecting into and through the arm *F*. The center of bulb and that of muffle as nearly as possible coincide. The bulb is held in position and free from the muffle by a clamp attached to stem on the outside of the furnace. The thermo-element is introduced through the opposite arm *E* in such a way that the junction may be contiguous with the air thermometer. The insulating tubulure is also supported by a clamp on the outside of the furnace. It is an essential part of the construction of the present apparatus that during rotation the muffle touches neither the air thermometer nor the thermo-element, both of which apparatus are stationary, and suspended quite free from all parts of the furnace.

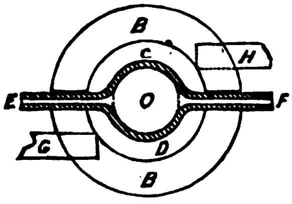


FIG. 36a. Elliptic revolving muffle; diagram.

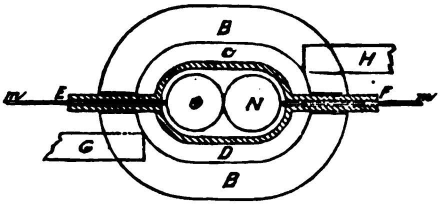
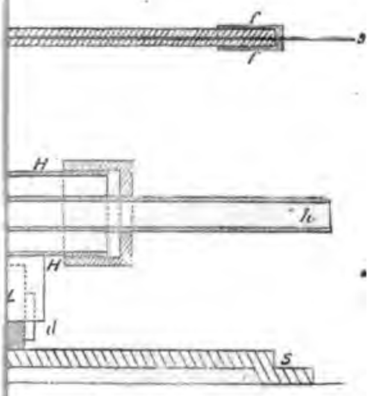


FIG. 36. Revolving muffle; diagram.

Having thus indicated the general principles of the constant temperature apparatus, I shall next describe the practical form of this furnace, which, after many trials, has been found satisfactorily serviceable.

This is given in front elevation and longitudinal section in Fig. 37 and in side elevation in Fig. 38, respectively, drawn one-fourth and one-half the actual size. The body of the furnace is shown at *B B B B*, a thick-walled cylindrical pot, surmounted by a hemispherical dome, *A A A*, the lid of the furnace. A central hole at *A′* and a series of six symmetric lateral holes, *a a*, *a a*, . . . in the lid are sufficient for the escape of the products of combustion.

The burners *H H H H* and *G G G G* project into the furnace as far as the inner surface. Their diagonal position is well shown in the side elevation (Fig. 38) and their internal construction in the longitudinal section of Fig. 37. Compressed air from a centrifugal blower, run by a one horse-power gas-engine, enters the central tubes *h h* and *g g*, respectively. The inlets of gas are shown at *c* and *c′*. Attached to the bottom of the burners are rectangular slides *I I* and *K K*, respectively, which pass through guides *L L* and *M M*. In this way the burners can be easily inserted or withdrawn from the furnace. A little pin, *d*, prevents their being inserted too far into the interior, and a similar longer pin or roller, *e*, is so adjusted as to rest the greater part or the whole of their weight upon the bed plate *S S*, instead of on the friable mass of the furnace. The burners shown in the figure were constructed entirely of gas pipe, and the disposition of parts is such as suggested itself after many trials. Burners in which back explosion is obviated by surrounding the mouths with a sieve or net-work of iron wire (as is the case in some of Fletcher's apparatus) are thoroughly unsatisfactory. These sieves obstruct the blast and are not as much a safeguard against back explosions as is necessary in an apparatus where constancy, or at least very uniform variation of temperature, is the requisite. In the blower of Fig. 37 the blast tube *h h* extends to within an inch of the mouth of the burner. The column of gas surrounds this tube. With the full current of air sent through the furnace the gas may therefore be as nearly cut off as is at all desirable, or it may be quite cut off without incurring any risk of explosion, either in the blower or in the burner. I may add that the tubes *c c* and *c′ c′* for gas supply should both point toward the more accessible side of the furnace, and there communicate with graduated stop-cocks, such as are furnished by the Buffalo Dental Company. For the furnace above half-inch supply-cocks are sufficient. The centrifugal blower which I used was of rather a smaller form than is usual in the market, being only about eleven inches in diameter and with paddles scarcely two and a half inches wide. It was taken from a portable forge. Doubtless even a smaller blower, i. e., a narrower blower, would have been desirable, so that the power of the engine may be spent in furnishing pressure of blast rather than quantity of air. The smallest form of Root blower (blacksmith's model) and larger forms of centrifugal blower had therefore to be discarded, for with the available power the blast obtained proved to be too large in quantity and too small in intensity. In the Root blower, moreover, the flame obtained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is intermittent, and in this respect objectionable. It will be well to state that the flame issuing at the mouth of the burner when the blast is cut off (a great torch fully two feet in length) is reduced to a blue cone scarcely eight inches in length for the maximum supply of gas. Placed in the position given the burners during the heating do not melt, but merely grow red hot at the mouth, and the oxidation is a minimum, because the general tendency is to reduce. It is well, however, to attach a reservoir of water behind the furnace and to tap it through lead piping and small faucets, so as to fall drop by drop upon the burners and thus prevent all possibility of superheating. In none of my experiments did ferruginous fluxing of the furnace body occur. I found in the experiments that to secure the maximum temperature desirable (say 1,400°), it was not necessary to open the half-inch clear-way cocks more than one-third. From this downward the intensity may be diminished to the merest ribbon of flame, sending in reality only a vortex of hot air through the furnace. Indeed this adjustment is very satisfactory, so that with an accurately graduated arc attached to the cocks it is possible, after the necessary preliminary measurements have been made, to open it in such a way as to strike any given temperature with some nicety. The cupola $A A$, which can be lifted off from the body $B B$, along the plane $A A$, emphasized in Fig. 38, has a suitable handle arrangement attached to it, which is omitted in the figure.

Having thus given a furnace which can be heated to any reasonable degree of temperature with extreme ease and convenience, I proceed next with the description of the revolving muffle. The muffle proper is shown at $E C D F$, in Fig. 37, and consists of two identical halves of refractory fire-clay, each of which is a hemisphere with two diametrically opposite guttered arms. The two halves are placed together, with their plane faces contiguous, but without cement. They are held together by surrounding their ends with appropriate collars of iron, $N N N N$ and $N' N' N' N'$, the outer edges of which are widely flanged. These flanges, $P P$ and $P' P'$, are turned circularly, with their circumferences carefully beveled, so as to fit nicely into the grooves of two pairs of friction-rollers, $Q Q$ and $Q' Q'$, of which $R R$ and $R' R'$ are the respective axes. Here I may well say that it is difficult to bake the muffle in such a way that the plane faces are not warped. Moreover, the two tubes, when placed together, show rather an elliptic ring-shaped section than a circular one, as is represented, with a little exaggeration perhaps, at $f f$, Fig. 38. But this irregularity furnishes an exceedingly satisfactory way of fastening the muffle into the collar. For if the width of the bore be so chosen as to fit snugly on the major diameter of the axle of the muffle, a flat ⌒-shaped spring of steel may be inserted in each narrow space between axle and collar, against the bulge of which (spring) set-screws $t t t t$, sunk into an equatorial rib of the collar, press as firmly as is permissible; or this space may be filled with fitting knife-edged blades of steel, or with asbestus board, against which the screws t press. All of these methods are good. Even when the temperature is so high as to fuse the inner surface of the collar the screws t can be worked loose with a drop of oil or petroleum, and after removal show no serious injury. It is not easy to fit the axle of the muffle into the iron collar, because the silicious material does not yield easily to the file. It may, however, be ground on a grindstone, or, with greater advantage, by filing it with a piece of its own substance.

Having thus shown how to fasten the collars symmetrically, and at such a distance apart that the opposed flanges may fit in the grooves of the opposed rollers Q, Q and Q', Q', it is next in order to describe the adjustment of the rollers themselves. Their axles, R, R, R', R', are mounted at suitable distances apart on a rectangular rod of cast-iron, u u, provided with a handle of wood, W. The rods u u, u' u' again are each adjustably fastened to Y shaped uprights Y, Y, Y, Y,[1] and Y', Y', Y', Y' by aid of strong screws V, V'. Loosening V or V' the rod u u or u' u' may be raised or lowered or rotated around the center of V or V' and clamped in any desired position. It is in this way that the inner edge of the collars N N N N, N' N' N' N' may be nicely adjusted with reference to the lateral shouldered holes of the furnace through which the axle of the muffle projects. Rotation therefore takes place on the friction-rollers, in which the wheel or flange P P rolls smoothly. It will be seen that some such arrangement as this is essential, for the rolling parts must be placed so far away from the hot parts that they may be lubricated. At very high temperatures the muffle becomes more or less viscous, and hence it is necessary to obviate all such tendencies to twist or wrench off the axles as an imperfectly oiled mechanism constantly presents. There is one further adjustment to be made: After the firing neither do the axles of the muffles coincide in prolongation, nor are the axes of the cylinders straight lines. Hence the axles of the rollers R R, R' R' are long cylindrical rods along which the rollers Q Q Q Q may slide laterally, their extreme positions being fixed by four adjustable set-screw collars x, x, x', x'.

To revolve the muffle a belt-pulley of wood Z Z has been screwed to the flange-wheel P' at a little distance from it. Over this passes round-leather belting, and the power is communicated by a corresponding pulley on a lateral shaft of the engine. The wooden belt-ring Z Z is far enough away from the hot parts to escape being charred. The belt, however, must be provided with a tightener.

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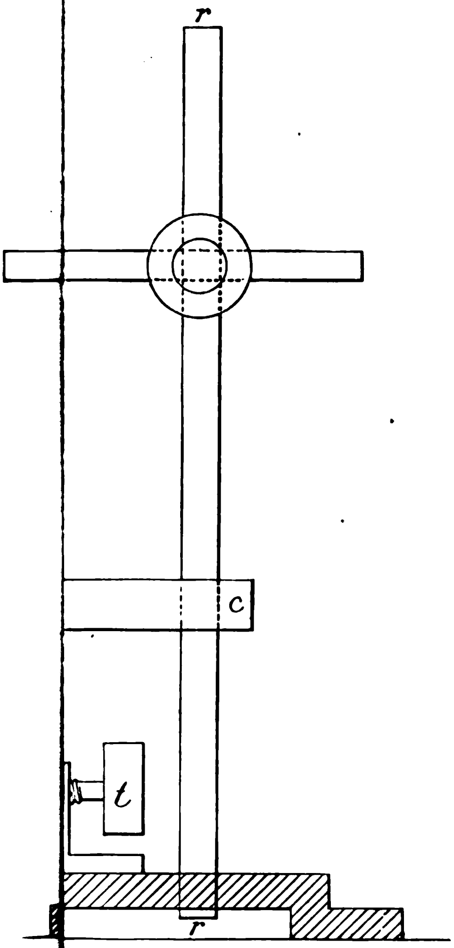
[1] The uprights were given the Y-shaped form to prevent the possibility of lateral slipping of the muffle. In later experiments I found this safeguard unnecessary, so that a simple flat upright, with a vertical slot opening upward to admit the screws V, V', is far preferable. In other words, the uprights in the figure are to be sawed off square above the slot. By this means greater facility of adjustment is secured when the collar is to be fitted to the axle of the muffle or removed from it.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Finally, the figure shows the air thermometer *f f k i e* in position, supported by the universal clamp *m m* attached to the vertical rod *q q*. A similar universal clamp, *n n*, on the opposite side of the furnace supports the insulator of the thermo-element *k k*. The clamp *n n* attached to the rod *r* should be a spring, so that elements may easily be either inserted or withdrawn. The ends of the wires of the thermo-couple appear at α and β and pass thence to a petroleum bath of known temperature, where they are suitably connected (page —) with the terminals of the measuring apparatus. The junction of the thermo-element is in contact either with the external surface or with the closed end of the re-entrant tube, according to the form of porcelain bulb selected. Of this further mention will be made. It is here in place to state the method of inserting the air thermometer, a method which must be convenient and expeditious. Supposing the collars $N \ldots, N' \ldots$ to be removed the air-thermometer bulb is covered properly by the two halves of the muffle. The collars themselves are completely cut through on one side by a slit between two nearly contiguous axial planes, which slit passes through the flange *P P*, as shown at *s n* in Fig. 38, as well as through the body of the collar, and is quite large enough to admit the capillary platinum tube of the air-thermometer. This slit does not seriously weaken the collar, strengthened as it is by the central rib into which the screws *t* are sunk, and by the flange *P P*. In this way the collar at the air-thermometer end of the muffle may be slipped on quite as readily as the other. Having therefore centered the muffle, as described above, it is then easy to fix and center the air thermometer, so that it may be quite free from contact with the muffle. In the case where a soldered air-thermometer of the form Fig. 33 is used, a muffle of an axis sufficiently wide to accommodate the neck must be used. A muffle of this kind is given in section in the diagram, Fig. 36. In place of adjusting the muffle it is often desirable to adjust the furnace. This may be done by four set-screws, *t t t t*, Fig. 38, which act in pairs at right angles to each other. An oil-dropper, by which the roller *Q* may be kept lubricated, is a desirable addition. Some such non essential parts are omitted in the figure to prevent confusion of lines.

Remarks regarding the apparatus and manipulation.—Bearing in mind that this furnace is as nearly as is practically convenient or possible the outcome of a theoretical principle for the construction of constant-temperature apparatus, that all manipulations to be applied may be made safely and with expedition, it is well to summarize the advantage gained, as well as to allude to such others as are easily within reach. The maximum temperature obtainable is indefinitely high, much higher than can be defined by porcelain air-thermometer measurements. Any other temperatures below this extreme value can be obtained with requisite constancy. If these intermediate temperatures be in the region of red heat it is simply necessary to diminish the supply of gas by partially closing the gauge stop-cock. If the temperatures be below red heat the gas may be shut off altogether, and the furnace closed by shutting the flue holes with a fire-clay plug or with asbestus. If all influx of air is cut off the furnace (below 500°) cools very slowly. During these stages of cooling it is not undesirable to continue a rotation of the muffle at a rate sufficiently slow to prevent currents of air from entering the polar parts and being hurled off centrifugally at the equatorial parts of the muffle. Here it is well to mention that the speed of rotation usually employed in the present experiments was about fifty revolutions per minute. Possibly this rate is too great, particularly at very high temperatures, at which the muffle becomes incipiently viscous, and much slower rates are therefore preferable. Protected from direct flame by the muffle, the fragile porcelain bulbs are heated with great regularity, and the liability of the thermometer to breakage is therefore nil.

In order to determine the constant of the air thermometer (zero reading) it is sufficient to place a mercury normal thermometer in contact with the bulb (or better in the central tube of the re-entrant bulb) in the cold furnace before heating. The same operation must be repeated in the cold furnace after heating. The difference of zero readings thus obtained is a test of the validity of measurement, inasmuch as it shows whether during the course of the comparisons the bulb has remained of fixed normal volume and whether air or gas has leaked into or out of the air thermometer. The mercury thermometer is inserted and held in position by the same spring-clamp which, during calibration, holds the thermo-element. In the form of bulb, shown in Fig. 32, to which most of the present remarks apply, the mercury bulb is pushed quite into the re-entrant tube and an identity of environment of mercury and air thermometers is thus secured. Of course it is more nearly accurate, though less convenient, to submerge the bulb in water of known temperature in order to get the zero or fixed point. All this will be discussed below.

During the heating of the furnace to white heat, the hollow axles, which necessarily lie in the circumambient sheet of flame, are heated more easily and kept at a greater intensity of red heat than the body of the muffle. This is the objectionable feature, due to the absence of the third rotation referred to on page 182. But this error, thus introduced, is confined to a small part of the stem; it does not extend as far as the muffle, in the interior of which, moreover, the hot air is churned around the bulb by the rotation; its harmful effect is fully obviated by the use of the re-entrant bulb, in which heat is communicated to the thermoelectric point junction through the surface of the air-thermometer bulb; it is entirely absent during the cooling of the furnace, conditions under which most of the experiments are made. Finally, the furnace has been so made that the zone of variable temperature, which surrounds the stem of the thermometer, is as narrow as possible when measured along the length of the stem. Indeed, the correction to be applied for the part of the porcelain stem, which has varying temperature, is almost nil. If, following Deville and Troost, a compensator is used to correct the stem error, this apparatus may temporarily replace the insulating tubulure of the thermo-element.

A final remark must be added with reference to silicification[1] of platinum. If the wires of the thermo-element be in contact with the surface of the air thermometer, and the temperature high enough to make the glaze appreciably viscous, the platinum is invariably attacked and destroyed as far as it is in contact with the glaze, and it is found embedded in it after cooling. The apparent effect is fusion, for the platinum thus silicified fuses at a temperature below that of the glaze. Quite aside therefore from the change of constants silicified platinum is unavailable for high-temperature measurement, because of its fusibility. Care must therefore be taken to avoid unnecessary contact of the thermo-electric wires with the glazed bulb, which is fortunately feasible, because the operator is able to see into the furnace as far as the air thermometer through the hollow axle at the side of the muffle on which the thermo-couple is inserted.

One great advantage enjoyed in using the present furnace is this, that even in case of extremely high temperatures it is possible to approach very near it without discomfort. The temperature of the exterior surface does not exceed 300°, and may be even further reduced by appropriate jacketing of asbestus. Hence all manipulations near the furnace can be conducted with facility. In the case of the large furnaces, described in Chapter I, the radiation from the furnace is intense, and all close approach to it is difficult.

A sketch of a revolving muffle for the comparison of two air thermometers, containing either two distinct gases, or the same gas at different temperatures, is given in Fig. 36*a*, where *B B* is the body of the furnace, *H*, *G*, the two burners, *C D* the revolving muffle, and *O* and *N* the two air densities to be compared. The revolving muffle is ellipsoidal in shape, and the appurtenances are the same as those described above. The stems of the air thermometers project at *m* and *m*, and capillary tubes connect each with the respective manometer. In the comparison of air thermometers both the expansion of the porcelain and the stem error compensate each other, and the data are thus as accurate as the environments are identical.

Finally, I desire to make a few remarks on the complete disposition of apparatus, as given in the frontispiece. The lower part of the figure

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[1] The tendency of platinum to combine with silicon, forming very fusible products, has long been known. Tait, endeavoring to use a bath of fused silicates for constant temperature, found the platinum wires, which he submerged therein, disintegrated. More recently, Colson (C. R., xciii, 1881, p. 1074; C. R., xciv, 1882, p. 26); Violle (C. R., xciv, p. 28); *Pernolet* (C. R., xciv, 1882, p. 99), have given especial prominence to this and similar phenomena. In these cases there seems to be a diffusion of the solids into each other, and the melting point of silicified platinum may be reduced to that of glass. I have often found platinum wire fused on or even embedded in the glaze of the air-thermometer bulb.

shows the position of the one horse-power gas-engine, to the left of which is the small centrifugal blower and to the right the bellows. The latter are worked by a short crank attached to the axle of the fly-wheel, and the blast obtained is small in quantity but high in pressure. The furnace-table completely surmounts the engine and carries on the left side (under *D*) a series of three or more small furnaces, resting on a special table of their own. These furnaces, fed by gas and the pressure blast of air from the bellows, contain crucibles of the form (Figs. 14 and 15) above, and are used for boiling-point measurements. Thermo-elements are inserted from below and held in position by a suitable clamp. Observations and manipulations are made in the way carefully detailed in Chapter II. On the right side of the furnace-table (under *C*) is fixed the revolving muffle-furnace, the parts of which have just been described, and are therefore easily recognized.

Quite to the right of the engine (under *B*), and screened from it by a wide board, is the manometric apparatus of the air thermometer (cf. page 209, below). The bulb and manometer are connected by a platinum capillary tube. A similar platinum tube connects the compensator with its manometer. Above the furnaces is an iron tube, through which the small furnaces may either be supplied with hydrogen or may be exhausted, as desired, the other end of this tube being simply attached to appropriate gasometric apparatus.

A set of air-thermometer bulbs are shown on a little shelf under *A*. The two vertical bulbs are of porcelain, being the forms Figs. 32 and 33 above. The oblique bulb is a re-entrant air thermometer of glass.

CONSTANT-VOLUME THERMOMETER—METHOD OF CALCULATION.

The general equation.—It has already been suggested that it is expedient to choose such methods of thermometry in which the degree of constancy of the zero reading before and after the high-temperature calibration may afford a guaranty of the reliable character of the results obtained. This test can well be applied when the constant-volume method is used. If the work be done with low pressures (<1 atmosphere) it is also possible to adjust the quantity of air that at such temperatures at which porcelain tends to become viscous the tension of the inclosed heated gas may approach that of the atmosphere.

The most general expression for the variables involved in any case of air thermometry may be rigorously put

$$\Sigma\left[V\left(H\frac{1+\beta T}{1+\alpha T}-h\frac{1+\beta t}{1+\alpha t}\right)\right]=A \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{I})$$

where V, V', V'' . . . are zero volumes whose special temperatures are T, T', T'' . . . for the pressure H, and t, t', t'' . . . for the pressure h, where A is proportional to the excess of volume at T over that of the fixed mass of gas at t, and where α is the coefficient of expansion of the gas and β the coefficient of cubical expansion of bulb, stem, etc. The equation assumes that the gas is perfect and that the bulb expands proportionally to its temperature. The equation is sufficient for the calculation of any one of the variables involved, supposing all the others to be known. In the method of constant volume, $A=0$.

In high-temperature measurement there are at least three parts of the air thermometer to be considered. The first of these is the hot region, and includes the bulb and the part of the stem at the same temperature; the second is the part of the stem in which temperature varies from the high value to that of the atmosphere; the third is the part in which the temperature is practically that of the atmosphere, and it includes the cold part of the porcelain stem, the capillary tubes, and the space of cold air above the meniscus of mercury. The whole of this may be appropriately called the cold part of the stem. It is obvious that the corrections to be applied are specially important when the temperatures of the bulb are high and the air is employed originally under small pressure. It is therefore expedient to derive the rigorous expression for temperature in terms of all the variables involved, and from this to derive a safe practical form by simplification.

The full expression in question introduces variables which may be symmetrically put as follows:

$$\begin{array}{cccc} h & H & V & \alpha \\ t & T & v' & \beta \\ t' & T' & v'' & \\ t'' & T'' & & \end{array}$$

where h is the tension of the gas at the lower temperature, t of the bulb, and t' and t'' of the variable and cold parts of the stem; where H is the tension of the gas at the high temperature, T, of the bulb, and T' and T'' of the variable and cold parts of the stem; where v is the volume of the bulb and hot stem, v' the volume of the variable stem, and v' the volume of the cold stem, all at zero degrees; where α, finally, is the coefficient of expansion of the gas, and β the coefficient of expansion of porcelain. The relation between these variables may then be rigorously expressed by the formula

$$T=\frac{1}{\alpha}\,\frac{H-h\dfrac{1+\beta t}{1+\alpha t}+\sum\left[\dfrac{v'}{v}\left(H\dfrac{1+\beta T}{1+\alpha T'}-h\dfrac{1+\beta t'}{1+\alpha t'}\right)\right]+\beta HT}{h\dfrac{1+\beta t}{1+\alpha t}-\sum\left[\dfrac{v'}{v}\left(H\dfrac{1+\beta T'}{1+\alpha T'}-h\dfrac{1+\beta t'}{1+\alpha t'}\right)\right]} \quad . \; . \; (1)$$

where the symbol Σ denotes that similar expressions occur additively for each $\frac{v'}{v}, \frac{v''}{v}, \frac{v'''}{v} \ldots$, to be considered, two of which, however, have been deemed sufficient.

The equation simplified.—To simplify this formula we replace $h\frac{1+\beta t}{1+\alpha t}$ by h_0, or the tension which would be observed if the bulb were placed in melting snow. Equation (1) then becomes, after solving for T,

$$T=\frac{H-h_0+\Sigma}{\alpha h_0-\beta H-\alpha\Sigma} \quad \ldots\ldots\ldots \quad (2)$$

where Σ stands for the whole bracket [ ] of equation (1). This equation is still rigorous, but it is very inconvenient for calculation. An equally rigorous but much more serviceable form is obtained by introducing T into the corrective member coefficiented by Σ. In this way equation (3) results

$$T=\frac{H-h_0}{\alpha h_0-\beta H}\left[1+\frac{1+\alpha T}{H-h_0}\Sigma\right] \quad \ldots\ldots \quad (3)$$

a form which is still rigorous, but may be conveniently used in practice with any desirable degree of approximation, as will presently appear.

In equation (3) Σ has the form

$$\frac{v'}{v}\left[H\frac{1+\beta T'}{1+\alpha t'}-h\frac{1+\beta t'}{1+\alpha t'}\right]+\frac{v''}{v}\left[H\frac{1+\beta T''}{1+\alpha T''}-h\frac{1+\beta t''}{1+\alpha t''}\right] \quad \ldots \quad (4)$$

which may be further simplified. Fortunately $\frac{v'}{v}$ is very small, for the mean temperature T' is only determinable with rough approximation.

I will define τ' by the equation

$$H\frac{1+\beta T'}{1+\alpha T'}-h\,\frac{1+\beta t'}{1+\alpha t'}=(H-h)\frac{1+\beta\tau'}{1+\alpha\tau'} \quad \ldots\ldots \quad (5)$$

and then use τ in a simplified form of Σ. In the second term of the form (4) $T''=t''$ very nearly. If, finally, $H-h_0$ and $H-h$ be regarded identical, equation (3) reduces finally to the approximate practical form

$$T=\frac{H-h_0}{\alpha h_0-\beta H}\left[1+(1+\alpha T)\left(\frac{v'}{v}\frac{1+\beta\tau'}{1+\alpha\tau'}+\frac{v''}{v}\frac{1+\beta t''}{1+\alpha t''}\right)\right] \quad \ldots \quad (6)$$

in which the terms $\beta\tau'$ and $\beta t''$ may also be neglected, as is obvious at once.

Error of the approximation.—It next becomes necessary to determine the numerical importance of the approximation just made, viz, the approximation in equation (5), and furthermore $T''=t''$, $H-h_0=H-h$, $1+\beta\tau'=1+\beta t''=1$ in the correctives. It also is necessary to investigate the effect of the individual variables of measurement on the result. Regarding the quantity $H-h$ it is obvious that its value will be at once $H-h_0$ when the bulb is surrounded by melting snow, as is usual. To obtain the value of the other approximations I refer to Tables 41, 42, and 43 for the capacities of bulbs and stems. Moreover, an inspection of Fig. 37 shows that the 40^{cm} of stem and 150^{cm} of capillary tube may be subdivided into parts, of which the first 5^{cm} of stem nearest the bulb have the temperature T of the bulb, and the 25^{cm} of stem, which project out of the furnace, together with the capillary tubes and spaces, have the temperature t'' of the air. The intermediate 10^{cm} of stem have a varying temperature between T and t'', the mean value of which has been symbolized by τ''. Hence the following volumes v, v' v'' occur in the correctives:

$$\begin{array}{lll}
v = & 300^{cc} & \text{(Table 43)} \\
v' = 0.0116\times 10 & = 0.116 & \text{(Table 43)} \\
v'' = \left\{\begin{array}{l} \text{stem, } 0.0116\times 25 \\ \text{copper-cap tube, } 100\times 0.0034 \\ \text{platinum-cap tube, } 50\times 0.0025 \\ \text{meniscus, } 0.4\times 1.22 \\ \text{glass cock, } 0.2\times 0.13 \end{array}\right\} & = 1.27 & \begin{array}{l} \text{(Table 43)} \\ \text{(Table 41)} \\ \text{(Table 42)} \\ \\ \\ \end{array}
\end{array}$$

whence it appears that

$$\frac{v'}{v}=0.00039 \qquad \frac{v''}{v}=0.00423.$$

With these data in hand it is expedient to return to formula (6), with the object of disposing of the corrective $\varkappa'=(1+\varkappa T)\left(\frac{v'}{v}\frac{1+\beta\tau'}{1+\alpha\tau'}\right)$. Assuming for a moment that $\tau'=\frac{1}{2}T$, there follows

TABLE 44.

T	$\varkappa'$
0	
100	0.00045
500	0.00057
1,000	0.00063
1,500	0.00067

Hence the error $\varkappa'$ is less than 1 : 1000, and it follows reasonably that τ' may be replaced by $\frac{1}{2}T$ without affecting the result more than $\frac{1}{100}$ per cent. The second corrective $\varkappa''=(1+\alpha T)\frac{v''}{v}\frac{1+\beta t''}{1+\alpha t''}$ is of greater consequence, and must be carefully evaluated in each experiment. The practical method consists in calculating an auxiliary table of double entry for $\varkappa'+\varkappa''$, in which the arguments are T and t''. T in such a table is to vary by successive steps of 100° each, t'' in steps of 10°. From this table, computed once for all, the corrective for any value of T and t'' may easily be taken by graphic or linear interpolation. By way of example, the following data for $\kappa'+\kappa''$, taken from tables of the kind in question, may here be inserted:

TABLE 45.—*Values of $\kappa'+\kappa''$ for divers T and t''.*

	$T=$			
	100°	500°	1,000°	1,500°
$t''=10°$	0.0060	0.0121	0.0197	0.0272
$t''=20°$	0.0058	0.0117	0.0191	0.0263
$t''=30°$	0.0057	0.0114	0.0185	0.0255

This table shows at once that if T'' and t'' differ by only a few degrees, the effect on the result will be less than $\frac{1}{100}$ of one per cent. per degree of difference of T'', and t''. Now, the walls of the furnace were purposely chosen thick. They are well jacketed, and it is therefore possible to screen off the radiation from the "cold" 25$^{\text{cm}}$ of stem entirely. The use of capillary tubes of metal enables the operator to place the manometer at some distance from the furnace and in an environment of constant temperature. The high furnace table conduces to this purpose, since the mercury apparatus may be expediently placed below and on one side of the furnace plane, quite screened from it by the table. Hence the approximation $T''=t''$ involves no greater error than a few hundredths of one per cent.

From these considerations the practical convenience of equation (6), when many values of T are to be reduced, appears at once. T computed simply as $(H-h_0)\ (\alpha h_0-\beta H)$ is in the extreme case within 3 per cent. of the correct result. By introducing this value into the corrective $\kappa'+\kappa''$ the effect on the result (T) is in the extreme cases less than $\frac{5}{100}$ of one per cent. Having therefore calculated a table of double entry for

$$\kappa'+\kappa''=(1+\alpha T)\left[\frac{v'}{v}\,\frac{1+\beta\frac{T}{2}}{1+\alpha\frac{T}{2}}+\frac{v''}{v}\,\frac{1+\beta t''}{1+\alpha t''}\right]\quad\cdot\ \cdot\ \cdot\ \cdot\ \cdot\quad(7)$$

of which the variables are T and t'' in the manner suggested, the approximate value $T_1=(H-h_0)\ (\alpha h_0-\beta H)$ may be corrected at once. It is in the interest of expeditious calculation moreover to compute a smaller table for βH. Mention has been made that h_0 is a mean value of measurements made before and after the calibration.

Compensator.—This is an ingenious device of MM. Deville and Troost, by which the stem error may be corrected directly. A second stem closed at one end, but otherwise identical in diameter, length, caliber, etc., with the stem of the air thermometer, is exposed simultaneously with it. The two stems are placed contiguously and so as to be in the same environment. MM. Deville and Troost, using volumetric methods, exhaust the air from the closed auxiliary stem by means of a Sprengel pump. The correction follows from the measured amount of air exhausted. I have used the compensator advantageously in the constant, volume method by connecting it with a special small manometer of its own. The principle for the reduction of the measurements by means of this apparatus follows easily when it is remembered that the compensator is in the practical instance an air thermometer, the volume of the bulb of which is zero. Applying therefore the general equation (1) above, I have at once for the air thermometer

$$v(HK-hk)+v'(HK'-hk')+v''(HK''-hk'')=0 \quad . \quad . \quad . \quad . \quad (8)$$

and for the compensator

$$v'(H_1K'-h_1k')+v''(H_1K''-h_1k'')=0 \quad . \quad . \quad . \quad . \quad (9)$$

where H_1 and h_1 are the tensions which correspond in the compensator to H and h of the air thermometer, and where K, K', . . . and k, k', . . . are abbreviations for the functions

$$\frac{1+\beta T}{1+\alpha T}, \frac{1+\beta T'}{1+\alpha T'}, \ . \ . \ . \ \text{and} \ \frac{1+\beta t}{1+\alpha t}, \frac{1+\beta t'}{1+\alpha t'} \ . \ . \ .$$

respectively. If the first equation be multiplied by H_1 and the second by H and the resulting equations be then divided by vH_1 there follows

$$(HK-hk)+\left(H\frac{h_1}{H_1}-h\right)\left(\frac{v'}{v}k'+\frac{v''}{v}k''\right)=0 \quad . \quad . \quad . \quad (10)$$

and since $k'=k''$ very nearly

$$(HK-hk)+\left(H\frac{h_1}{H_1}-h\right)k'\frac{v'+v''}{v}=0 \quad . \quad . \quad . \quad (11)$$

for which, with an error less than 0.2 per cent. at 2,000°, T may be deduced as follows:

$$T=\frac{1}{\alpha-\beta}\,\frac{1-\left[\frac{h}{H}k-\frac{v'+v''}{v}\left(\frac{h_1}{H_1}-\frac{h}{H}\right)k'\right]}{\left[\frac{h}{H}k-\frac{v'+v''}{v}\left(\frac{h_1}{H_1}-\frac{h}{H}\right)k'\right]}.$$

Here the variable temperature T' is eliminated.

By the use of the compensator the discrepancies due to porosity of porçelain, to fissures and other irregularities, may be partially obviated. It may be made to subserve another important purpose, viz, to measure $v'+v''$, the true volume of the stem and capillary connections. To do this it is merely necessary to connect the compensator with the manometer, as has been explained with reference to the air thermometer, in such a way, however, that the variable space above the upper meniscus of the manometer (see Fig. 30) may be read off in cubic centimeters. The volume v_0 in question is then at once determinable volumetrically. For if p' and p'' be the tensions corresponding to the volumes v_0+v' and v_0+v'' for the same mass of air, under constant temperature, then

$$v_0=\frac{p'v'-p''v''}{p''-p'}.$$

The apparatus actually used was a burette of 50^{cc} capacity, reading to within 0.1^{cc}, and which had been carefully calibrated. The lower end of this was connected with the flexible hose of the manometer, the upper end with the platinum capillary tubes leading to the stem. By aid of an interposed stop-cock (see page 170) the quantity of air in this system of tubes could be varied at pleasure. In the table following I give the results obtained, from which the general character of the measurement may be learned. v and p are the corresponding values; v' and p' or v'' and p'', respectively, and v_0 the zero volume of this set of canals above the fiducial mark. "Length" and "Diameter" refer to the porcelain stem:

TABLE 46.—*Compensator volumetry.*

No.	v	p	v_0	Length.	Diam.	Remarks.
	cc.	*cm. Hg.*	*cc.*	*cm.*	*cm.*	
a	0.30	77.49	1.7	....	0.8	The repetition of this series leads to practically the same result.
	2.30	38.98				
a	0.70	66.94	1.6	....	0.8	
	3.50	30.32				
a	1.05	57.40	1.8	....	0.8	
	5.53	22.27				
a	1.57	48.21	1.9	....	0.8	
	9.00	15.42				
a	0.27	76.46	1.7	....	0.8	
	16.50	8.31				
b	0.30	76.50	3.45	32	0.8	
	15.40	15.48				
b	0.50	75.16	3.40	32	0.8	
	15.40	15.60				
1	0.12	75.40	2.35	40	0.8	
	3.65	30.65				
	0.40	68.69	2.28	40	0.8	
	3.60	30.78				
	6.00	31.13	2.39	40	0.8	New adjustment.
	1.02	76.59				
	8.62	23.90	2.43	40	0.8	
	1.03	76.59				
	3.85	32.75	2.03	36	0.8	Do.
	0.48	76.65				
	0.58	76.03	1.91	36	0.8	
	4.28	30.57				

TABLE 46.—*Compensator volumetry*—Continued.

No.	v	p.	v_0	Length.	Diam.	Remarks.
	cc.	*cm. Hg.*	*cc.*	*cm.*	*cm.*	
2	0.32	76.02	2.20	40	0.8	
	4.46	28.80				
	4.50	28.87	2.16	40	0.8	
	0.30	78.13				
3	0.85	75.85	1.31	40	1.0	
	4.45	28.44				
	5.44	21.80	1.47	40	1.0	
	0.65	81.05				
4	5.20	29.66	1.20	40	1.0	
	1.20	79.20				
	1.20	79.12	1.21	40	1.0	
	8.23	20.16				
	0.30	53.89	1.06	40	1.0	New adjustment.
	3.44	16.28				
	3.50	16.39	1.11	40	1.0	
	0.22	56.85				
	3.54	31.37	1.16	40	1.0	Do.
	0.80	75.13				
	1.65	38.23	0.55	....	....	Platinum capillary tubes and glass stop-cock, without porcelain stem.
	0.52	78.55				
	2.15	30.68	0.52			
	0.52	78.61				
	0.13	76.17	0.52			Platinum capillary tubes and glass stop-cock, without porcelain stem; new adjustment.
	1.82	21.19				
	0.20	69.54	0.49			
	1.60	23.03				
	3.35	31.85	0.53	....	....	Do.
	1.10	75.82				

The errors in these results are about 0.1^{cc}, and they are easily referred to microscopic leaks, to variations of temperature, and to the possible occurrence of moisture in the stems.

From these data it appears, moreover, that the internal volume of stems 0.8^{cm} thick is not necessarily smaller than the internal volume of stems 1.0^{cm} thick. Hence the observed differences of volume between the divers stems are largely due to internal fissures, such as can not be detected, except by breaking the stems. It is interesting to note that the volumes measured volumetrically are not more than twice as large as those measured by weight calibration. Hence the superior limit of the errors in Tables 44 and 45 is not more than double the values there given.

Errors of measurement in general.—The degree of absolute accuracy with which the divers quantities h_0, H, α, β, $\frac{v'}{v}$, $\frac{v''}{v}$, must be measured in order that the effect on T may not exceed 1 : 1000 follows easily from the equation of errors

$$\delta x = \frac{dx}{dT}\,\frac{T}{1000} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

From this the following six special equations result, equations which are approximate and put in such forms as may best facilitate the computation:

$$\delta H = h_0 \frac{[\alpha-\beta(1+\alpha T)]^2}{\alpha-\beta}\,\frac{T}{1000} \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

$$\delta h_0 = -h_0 \frac{[\alpha-\beta(1+\alpha T)]^2}{(\alpha-\beta)(1+\alpha T)}\,\frac{T}{1000} \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

$$\delta\alpha = -\frac{[\alpha-\beta(1+\alpha T)]^2}{1000\,.\,\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

$$\delta\beta = \frac{[\alpha+\beta(1+\alpha T)]^2}{1000\,\alpha\,.\,(1+\alpha T)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

$$\delta\left(\frac{v'}{v}\right) = \frac{1+\alpha\frac{1}{2}T}{1+\beta\frac{1}{2}T}\,\frac{1}{1000\,.\,(1+\alpha T)} \quad . \quad . \quad . \quad . \qquad (17)$$

$$\delta\left(\frac{v''}{v}\right) = \frac{1+\alpha t''}{1000\,.\,(1+\alpha T)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

If into these equations we introduce $h_0=16^{cm}$, the value which obtains in most of the examples below; if, moreover, $\alpha=0.00367$ and $\beta=0.000017$, $t''=20°$, then formulæ (13) to (18) lead to the following tabular comparison. In the table both the absolute values of the errors δh_0, δH, $\delta\beta$, $\delta\left(\frac{v'}{v}\right)$, $\delta\left(\frac{v''}{v}\right)$, which give rise to an error of $T/1000$ in the result, as well as the relative errors $\delta\beta/\beta$, $\delta\left(\frac{v'}{v}\right)/\frac{v'}{v}$, and $\delta\left(\frac{v''}{v}\right)/\frac{v''}{v}$ are fully computed for a series of values of T.

TABLE 47.—*Comparison of divers errors which effect the result by* 1 : 1000.

T	δh_0	δH	$\delta\beta\times10^6$	$\delta\left(\frac{v'}{v}\right)\times10^6$	$\delta\left(\frac{v''}{v}\right)\times10^6$	$\frac{\delta\beta}{\beta}$	$\frac{\delta\left(\frac{v'}{v}\right)}{\frac{v'}{v}}$	$\frac{\delta\frac{v''}{v}}{\frac{v''}{v}}$
°	*cm.*	*cm.*						
100	−0.004	0.006	2.61	860	780	0.150	2.2	0.184
500	−0.010	0.028	1.27	660	380	0.074	1.7	0.080
1,000	−0.012	0.056	0.75	610	230	0.044	1.6	0.054
1,500	−0.013	0.083	0.53	580	170	0.031	1.5	0.039

Inasmuch as h_0 must be measured to 0.01^{cm} it is quite obvious that corroborative readings before and after heating are essential, and that the air thermometer during the intermediate measurements must be perfectly tight. Since the error decreases proportionally to h_0, the additional accuracy of greater zero tensions does not compensate the hurtful effect of high internal pressures at high temperature. Hence low pressures are preferable. Regarding H, it appears that rise or fall of temperature must not be so rapid that the retardation due to flow of gas through the capillary tubes maintain greater differences of pressure than 0.03^{cm} to 0.08^{cm} of mercury. A good cathetometer presupposed, it is not difficult to measure both h_0 and H with the accuracy here called for.

Under most favorable circumstances the error of T is as large as the error of α, a result which equation (15) approximately shows. The value chosen, 0.003665, is Regnault's[1] constant-volume value, and has been found experimentally for the interval 0° to 100°. The use of the same coefficient for temperature indefinitely high and for all tensions[2] is to some extent arbitrary. The error thence resulting may be estimated at as much as one-half of one per cent. The convenience with which the constant pressure method is available for measurements with gas differing widely in normal density is one of its most valuable features. The desideratum of an elliptic revolving muffle for the comparison of the gas thermometer data of different gases, when the temperature of the same environment is measured, has been suggested.

The unusually small coefficient of cubical expansion $\beta=0.000016$ to 0.000017, which MM. Deville and Troost found for the porcelain of Bayeux, makes the necessary accuracy of the coefficient β sufficiently attainable. The table shows that even in extreme cases, $T=1{,}500°$, an error of 3 per cent. in β is not serious, while the expansion coefficients of the metal and glass parts of the air thermometer need not be distinguished from β, because these parts are almost negligible here. This exceptionally small value of β is, however, only admissible in the case of thermometers which have frequently been heated. In the case of new thermometers these desirable qualities are vitiated by the occurrence of permanent expansion for each heating. In comparison with β this permanent expansion (permanent diminution of density) is unfortunately enormously large, aggregating in the first six heatings, for instance, as much as 1.5 per cent. Whenever temperature increases too rapidly the temperature, and hence also the volume of the bulb, is larger than corresponds to the mean temperature of the gas. The reverse of this takes place on cooling.

Conformably with the numerical results on page 197, Table 47 shows that $\frac{v'}{v}$ may be affected by an error of almost twice its own magnitude without seriously bearing on T, even in unfavorable cases. The importance of $\frac{v''}{v}$, however, increases rapidly as T increases, and must in un-

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[1] Regnault: Memoires de l'Inst., vol. 21, 1847, p. 91; ibid., p. 110.

[2] Cf. Literary Digest, pp. 36–38.

favorable cases be known within 4 per cent. These results are also in keeping with Table 45, above. Fortunately it is feasible to measure $\frac{v''}{v}$ with the accuracy here required, as well as to sufficiently exclude the effect of temperature.

A careful survey of the sources of error just discussed shows how exceedingly difficult the measurement of high temperatures, with an accuracy of 1 : 1000, really is. Quite aside from these discrepancies and the arbitrariness of α and β, the lag error, the environment error, the moisture error, the error due to the permeability of porcelain and to diffusion of some gases through it, and the error of unknown flaws, have yet to be discussed. In the face of these serious difficulties I was therefore pleased to find that greater harmony prevails in the established data for high temperatures than there was reason to anticipate at the outset. I may state here that a more rigorous discussion of errors is to be made in treating the constant-pressure method, since this method is very much better adapted for high-temperature measurement than the present one. I will (p. 228) give the methods of allowing for all arbitrary errors and such as are not considered here.

CONSTANT-VOLUME THERMOMETER—EXPERIMENTAL RESULTS.

Earlier results.—The measurements were commenced with the forms of bulb shown above in Fig. 32. These bulbs are not glazed internally, but consisting of but a single piece they can be manipulated with greater facility than the others, in which soldering must precede the temperature measurement. To obtain some idea of the availability of the unglazed bulbs, I made a number of measurements of the boiling point of water. Examples of the results obtained are given in Table 48, in which H and h_0 are the tension of the air at 100° and at 0° in centimeters of mercury. It is to be remarked that h_0 is here *directly* obtained by surrounding the bulbs with melting snow for many hours. By way of comparison, the same temperature T is also measured by a glass air thermometer.

TABLE 48.—*Moisture error of unglazed bulbs.*

No.	h_0	H	T	Remarks.
Glass:	*cm.*	*cm.*	*cc.*	
No. 1	76.70	104.47	100	
Porcelain:				
No. 1	73.50	141.90	256	Bulb not specially dried.
No. 2	72.40	115.00	162	Both bulbs dried by repeated exhaustion after calibration with water. Bulb at 100° during drying.
No. 3	76.46	119.58	155	
No. 4	72.62	102.98	115	Bulb carefully dried by repeated exhaustion with mercury air-pump. Bulb and stem at 100°.

The results of this table are startling. They seem to show that bulbs not glazed internally are worthless for temperature measurement. The error is very largely due to the presence of moisture in the bulbs; probably also to the condensation of air in the pores of the unglazed porcelain. An explanation of these results can be given by equation (13) and Table 48. This consideration exhibits an important principle, so far as drying by exhaustion is concerned, and may therefore be made here. Bulb No. 4, which is most carefully exhausted, need alone be discussed. It appears that the value of δH and δh_0, which give rise to an error of $\frac{T}{10}$, are approximately $\delta H = 2.7^{\text{cm}}$, and $\delta h_0 = 1.8^{\text{cm}}$. Now, after a mercury air-pump has been much used for drying, moisture is apt to show itself in the receiver, after which the exhaustion can not be carried further than 2^{cm} at ordinary temperatures. Hence it appears that unless the exhaustion be very frequently repeated a tension of aqueous vapor equivalent to about 2^{cm} of mercury at 100° may fail to be removed, an amount nearly sufficient for the discrepancy in question. It is to be noted that like errors in H and h_0 do not compensate each other. The amount of water thus remaining in the pores of the cold bulb is about 4^{mg}.

These results point out the desirability of perfect exhaustion and the necessity of keeping the air-pump dry. In view of the enormous discrepancies cited in the last table, the unglazed bulbs were discarded. Some years after, however, when the difficulty of soldering porcelain had been tried in many experiments, I resolved to test these unglazed bulbs again, with a view to perfecting them. In the first place it is obvious that if, instead of determining h_0 directly with melting snow, this datum be calculated from measurements of h made at ordinary temperatures (25°), better results will probably be obtained, since the small impurity of vapor may in the latter case be more accurately treated, like a gas. Moreover, care was taken to dry the bulbs at red heat prior to using them for air thermometry. Table 49 contains results for bulbs thus dried, all unglazed internally, except No. 1, which is the soldered form (Fig. 33), glazed internally.

TABLE 49.—*Moisture error of unglazed bulbs.*

No.	H	h_0	T	Remarks.
Porcelain:	*cm.*	*cm.*	°*C.*	
No. 1.......	75.8	94.2	99	
No. 2.......	75.7	94.3	99	
No. 3.......	62.6	78.9	102	
No. 2.......	35.7	45.7	104	
No. 3.......	48.5	61.1	102	
No. 4.......	76.3	97.0	102	
No. 4.......	17.26	21.60	101.1	Cathetometer measurement.

These results are such an enormous improvement on the discrepancies of Table 48 that it seemed expedient to endeavor to further investigate the behavior of these instruments at high temperatures. If under these conditions the bulbs show no greater variations than is in accordance with the above data, the further improvement of the bulb presents itself emphatically. Values of high temperatures sufficiently approximate for the present purposes are obtainable by the method investigated in Chapter II, where apparatus for calibrating thermo-elements with known boiling points are described. It seemed especially desirable to make this high-temperature comparison in order that some definite preliminary notion of the degree of accuracy of high-temperature data in general might be independently obtained. Examples of these results are given in the following tables, 50 and 51. The first of these (Table 50) contains a comparison of the calibrated thermo-element and air thermometer made in the large gas-muffle furnace described on page 181. The junction of the thermo-couple having been tied with asbestus wicking to the equatorial parts of the air thermometer, the whole bulb was thereupon surrounded with a non-conducting jacket of carded asbestus, from one to two inches thick, inclosed in a cylindrical asbestus box. Both the thermo-electric and the air thermometer measurements were made in time series, with one observer at each instrument.[1] In this way the rate of heating or cooling of the furnace appears among the results. As usual h_0 is the (calculated) zero reading of the air thermometer, H the corresponding reading at the high temperature T, and at the time given in the same horizontal row. Again, t is the temperature of the cold junction of the thermo-element, e the corresponding electro-motive force, in microvolts T_{hg} and T_{zn} the calculated (thermoelectric) temperature when in the first case the calibration is carried only as far as the boiling point of mercury, in the second case when carried as far as the boiling point of zinc. T_{hg} and T_{zn} are the results of graphic interpolation, as explained in Chapter II, page 114.

TABLE 50.—*Comparison of air thermometer and thermo-element.*

Bulb No. 3; $h_0=26.6^{cm}$			Thermo-couple No. 36.				
H	T	Time.	t	e_{20}	T_{hg}	T_{zn}	Time.
cm.	°*C.*	*hours.*	°*C.*	*microvolts.*	°*C.*	°*C.*	*hours.*
330.1	66	12.46	24.7	650	97	97	12.52
464.3	207	.53	.8	1530	196	196	.55
637.9	389	.57	.8	2220	264	268	.56
705.7	462	.60	.9	4270	443	460	.61
759.4	519	.63	25.0	6400	596	636	.71
817.1	581	.66	.3	7260	655	705	.79

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[1] Dr. Hallock kindly assisted me in this series of measurements.

TABLE 50.—*Comparison of air thermometer and thermo-element.*—Cont'd.

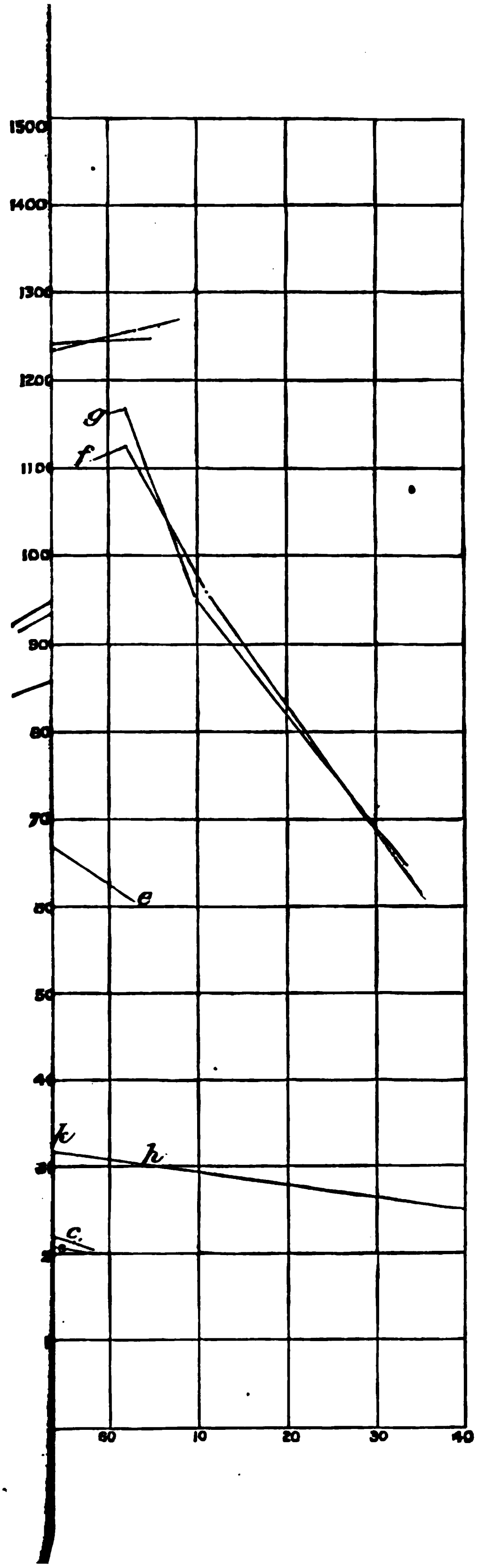
Bulb No. 3; $h_0=26.0^{cm}$			Thermo-couple No. 36.				
H	T	Timo.	t	e_{20}	T_{hg}	T_{zn}	Time.
cm	°*C.*	*hours.*	°*C.*	*microvolts.*	°*C.*	°*C.*	*hours.*
847.9	613	.69	.4	8490	732	792	.86
898.7	670	.74	.5	8860	755	821	.89
928.7	700	.79	.5	9200	777	845	.94
965.5	741	.83	.7	9710	802	878	1.00
1017.3	797	.90	.9	10110	826	906	.07
1078.5	863	1.01	26.3	10530	850	933	.17
1107.0	896	.08	.4	10760	864	950	.22
1150.6	942	.25	27.4	11570	908	1000	.45
1179.8	973	1.35	27.6	11630	911	1005	1.50
1187.8	984	.42	.7	11700	915	1010	.53
1198.8	996	.50	.9	11840	924	1017	.61
1202.8	1000	.58	28.2	11970	928	1026	.70
1203.3	1000	.67	28.4	12060	934	1030	.75
1202.8	1000	.75	......	......	......	......	......
Gas of furnace shut off 1.77^h							
1199.8	997	1.81	28.9	10780	864	951	1.87
1126.5	916	.87	29.2	9930	815	893	.91
1064.3	848	.92	29.3	9130	769	838	.96
979.3	756	.97	29.4	8520	733	794	.98
934.8	706	2.01	29.4	7570	675	727	2.03
859.3	626	.07	29.5	7050	640	686	.06
798.3	561	.13	29.5	6500	610	651	.09
721.9	478	.19	29.5	6190	584	621	.12
678.4	433	.27	29.5	5170	515	538	.21
633.5	385	.35	29.5	4700	476	496	.26
501.7	340	.43	29.4	4310	445	461	.30
555.4	302	.53	29.4	3980	421	436	.35
522.7	267	2.63	29.4	3400	372	384	2.44
483.9	227	.74	29.4	3140	348	358	.48
462.9	206	.91	29.4	2850	324	332	.54
			29.4	2310	274	277	.68
			29.4	2000	245	246	.79
			29.4	1790	226	226	.87
			29.4	1600	214	214	.93

The following comparison (Table 51) of the data of thermo-element and air thermometer was made in the revolving muffle, described on page 181. The simple round bulb (No. 4), not provided with a central tube, having been properly adjusted, the thermo-electric junction was placed nearly in contact with it. The table contains three independent series of measurements, and nomenclature used is identical with that of the foregoing table:

TABLE 51.—*Comparison of air thermometer and thermo-couple.*

Bulb No. 4.			Thermo-couple No. 37.				
H	T	Time.	t	e	T_{hg}	T_{m}	Time.
		(*a*)	$[h_0=16.74^{cm}]$				
cm.	°*C.*	*hours.*	°*C.*	*microvolts.*	°*C.*	°*C.*	*hours.*
82.2	1115	1.57	25.3	12920	980	1082	1.53
88.9	1238	1.85	25.8	14780	1073	1190	1.73
89.2	1244	1.93	27.3	15430	1102	1233	1.90
89.3	1246	2.03	27.3	15690	1115	1249	2.05
		(*b*)	$[h_0=14.70^{cm}]$				
62.6	923	2.27	26.3	10480	850	930	2.22
64.2	954	2.35	26.5	11020	878	972	2.33
72.5	1118	2.52	27.0	12250	944	1045	2.47
76.6	1202	2.62	27.3	14000	1034	1150	2.60
77.3	1218	2.65	27.8	14760	1072	1195	2.72
78.6	1244	2.73	28.2	15060	1085	1218	2.82
79.1	1254	2.80	28.2	14970	1081	1206	2.87
79.1	1254	2.82	28.5	14870	1075	1201	2.92
78.8	1248	2.85	....	....	....	....	....
78.4	1240	2.92	....	....	....	....	....
			Gas of furnace shut off.				
72.8	1126	3.03	29.0	12930	980	1085	3.03
66.8	1006	3.12	29.5	10710	861	945	3.17
62.8	927	3.22	29.6	10090	827	904	3.20
57.3	819	3.30	30.0	9040	765	833	3.32
51.4	704	3.47	30.6	7690	683	735	3.48
46.3	603	3.68	31.3	6490	604	644	3.68
42.0	519	3.92	31.8	5340	524	551	3.92
36.9	422	4.27	31.8	4130	430	449	4.27
32.5	337	4.08	31.8	3140	350	359	4.70
24.8	188	....					
			$[h_0=15.68^{cm}]$				
77.0	1115	2.00	29.0	14170	1042	1160	2.00
77.4	1122	.03	29.0	14270	1046	1166	2.03
68.5	957	.18	29.0	10770	865	948	2.17
52.7	659	.53	29.0	7090	644	690	2.50

The results of these two tables, 50 and 51, may best be compared graphically by regarding the various values of temperature as functions of time. This has been done in the chart, Fig. 39. The curves *a*, *b*, *c* correspond, respectively, to T, T_m, and T_{hg} of Table 50; the curves *h*, *k*, *i* to T, T_m, T_{hg}, of Table 51, respectively; the curves *f*, *g*, and *m*, *n* to T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and T_{xm} of the same table. The curves *d* and *e* are supplied by way of example, and are values of T_{xm} obtained by heating a Fletcher injector (muffle form heated by power blast) to maximum intensity and then allowing it to cool. A comparison of curves *a*, *b*, *c* shows that from 600° the heating takes place sufficiently slowly to make comparative measurements admissible. Throughout the stage of heating T and T_{xm} agree within 30°, usually much more closely, whereas T and T_{kg} differ by as much as 90°. The maximum temperature is not above 1,000°. After the gas is shut off the furnace cools too rapidly for calibration work, the thermo-couple cooling at somewhat greater rates than the air thermometer. The curves *d* and *e* for the muffle furnace, the form of which is a thick-walled cylindrical box, exhibit rates of cooling very much less than the curves *a*, *b*, *c*—a desideratum which is much more fully realized in work with the revolving muffle furnace, for which the curves *h*, *k*, *i* apply. Unfortunately, owing to accidents, the statistics of heating are only imperfectly shown; but beginning at about 900°, which is here nearly the maximum intensity for the amount of gas supplied, T and T_{xm} differ by only 10°, T and T_{kg} by about 80°. The curves then rise rapidly, owing to the fact that the influx of gas has been increased, until at 1,250° T and T_{xm} differ by nearly 40°, T and T_{kg} by nearly 150°. For reasons of a practical kind, the temperature was not increased above 1,250°. Below 1,000° cooling takes place at rates sufficiently retarded to make calibration work practicable. Above 1,000° it is expedient to obtain the different degrees of constant temperature by regulating the supply of gas. A comparison made between the curves *k* and *h* throughout the course of cooling leads to the inference that the well-known thermoelectric formula $e=a\tau+b\tau\sigma$ is insufficient for interpolation.

The extrapolated temperature T_{kg} differs enormously at high temperatures from its air-thermometer value, the latter being the greater. Since below 900°, $T<T_{xm}$, the discrepancy can not be referred to friction of gas in the capillary tubes, the effect of which would be of the opposite sign. The only cause which would tend to cool the air thermometer at a greater rate than the thermo-couple is the effect of the entrance of the air above the meniscus of the manometer, while the mercury is gradually moving upward from a lowered position into contact with the fiducial mark. Or, finally, the error $T-T_{xm}$ may indicate superheating in the calibration work.

It is by no means the object to furnish in this place more than a statistical diagram, as it were, of the degree of accordance, which the high-temperature measurements made in widely different ways, present.

When comparisons are made in the Bunsen muffle the ascending values of T_{xm} exceed the descending values of T_{xm} for the same T. The ascending and descending values of T_{xm} in case of comparisons made in the revolving muffle are nearly the same. This is a pretty fair test for identity of environment. Nevertheless, if all values of T_{xm} obtained be laid off as functions of T, the band or pathway thus obtained is in some instances nearly 100° wide and the boiling points of zinc fluctuate between 925° and 995°.

Later results.—Following the suggestion of the results contained on pages 199 to 204, I made the following series of additional comparisons. The bulb used is still the non-re-entrant form, not glazed internally. Great care was taken to dry it thoroughly by heating the bulb to 100°, and then exhausting the air to a few tenths millimeter. After being treated in this way the bulb was filled with air, dried over anhydrous phosphoric acid. In the last two series h_0 is calculated from the tension observed at 100°. Special care was taken with the cathetometric measurements. The series of temperatures is ascending. The influx of gas is gradually increased by means of a graduated stop-cock, and the calibration measurements are made after each increment as soon as the temperature has again become stationary. In this way not only may any number of degrees of constant temperature be obtained, but the mean rate at which temperature increases may be reduced as near zero as is desirable. If therefore one observer[1] notes the instant of contact between the upper meniscus of the manometer and the fiducial mark, the other observer may note the corresponding cathetometer reading of the lower meniscus for the same instant. From a comparison of the following results as a whole I infer that in proportion as the temperature of the muffle increases, equality of temperature for all points of its inner surface more nearly obtains. This is due to the fact that at high temperatures its heat conduction is better. For low temperature calibrations it is therefore advisable to use a muffle cooling from red heat in a closed furnace. In the tables e_{20} has been calculated for $t=20°$. The actual temperature (t) of the lower junction is given in Table 52 for each case.

TABLE 52.—*Comparison of air thermometer and thermo-couple.*

$h_0 = 14.66^{cm}$. Bulb No. 4.			Thermo-couple No. 37.		
H	T	Time.	t	e_{20}	Time.
cm.	°*C.*	*hours.*	°*C.*	*microvolts.*	*hours.*
27.35	241	2.78	28.0	2545	2.78
30.25	297	2.88	28.0	2941	2.84
31.68	324	2.99	28.0	3060	2.90
33.25	354	3.14	28.0	3283	2.97
34.32	375	3.35	27.8	3792	3.40
34.32	375	3.42	27.8	3780	3.43
41.47	512	3.73	27.8	3780	3.45
42.33	529	3.78	28.3	5475	3.68
48.49	648	4.00	28.3	5820	3.75
49.99	678	4.07	28.3	7132	3.93
50.86	694	4.11	28.3	7706	4.02
57.80	831	4.31	28.3	8015	4.08

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[1] Mrs. Anna H. Barus assisted me in this work.

TABLE 52.—*Comparison of air thermometer and thermo-couple.*—Cont'd.

$h_0 = 14.66^{cm}$. Bulb No. 4.			Thermo-couple No. 37.		
H	T	Time.	t	e_{20}	Time.
cm.	°*C.*	*hours.*	°*C.*	*microvolts.*	*hours.*
58.77	850	4.35	28.3	8254	4.12
59.55	866	4.43	28.8	10260	4.33
65.67	985	4.65	29.0	10357	4.37
67.88	1031	4.72	29.3	10459	4.43
69.95	1072	4.77	29.3	12622	4.68
			29.3	13472	4.75
			29.3	13902	4.78
28.92	271	1.43	27.8	3596	1.45
31.89	327	1.49	27.8	3925	1.50
33.58	360	1.53	27.8	4127	1.53
35.38	394	1.59	27.8	4457	1.60
37.10	426	1.68	27.8	4723	1.70
38.19	448	1.78	27.8	4847	1.78
38.77	459	1.87	28.8	5100	2.00
39.13	466	1.95	28.8	5100	2.03
39.45	472	2.03	28.8	6144	2.17
41.00	502	2.14	28.8	6507	2.20
45.46	588	2.27	28.8	7045	2.30
46.73	613	2.33	29.3	7281	2.37
47.87	635	2.40	29.3	7455	2.42
48.80	653	2.48	30.3	8270	2.75
50.18	680	2.58	30.8	8153	2.88
51.32	703	2.69	30.8	8872	3.00
51.29	702	2.85	31.3	9651	3.12
52.59	727	2.99	31.3	9910	3.17
54.81	771	3.08	31.8	10375	3.33
56.69	808	3.16	32.6	10289	3.50
58.56	845	3.28	33.0	13021	3.73
58.95	852	3.49	33.3	13423	3.83
65.49	982	3.69	33.8	13427	3.02
68.40	1040	3.79	33.8	14297	4.00
68.86	1049	3.87	33.6	14677	4.05
69.87	1070	3.98	34.3	15191	4.12
72.03	1112	4.05	34.3	15511	4.17
73.72	1146	4.10	34.3	15732	4.22
75.68	1186	4.17	34.4	15852	4.30
76.85	1209	4.22	34.6	15963	4.42
77.69	1227	4.26			
78.62	1245	4.33			
79.11	1255	4.39			
79.47	1262	4.44			

In spite of the care taken with these observations the results do not show the uniformity and accuracy expected; this appears from a graphic representation of the following correlative values, Table 53, taken from Table 52.

TABLE 53.—T and e_{20}.

I.		II.		III.	
T	e_{20}	T	e_{20}	T	e_{20}
250	2630	350	4050	960	1138
300	3050	400	4490	995	1176
375	3790	450	4860	1080	1340
525	5800	470	5100	1100	1378
670	7860	550	6560	1130	1445
860	10400	600	7050	1180	1520
1016	12850	630	7350	1240	1610
1080	13800	702	8240	1260	1628
		730	8860		
		820	10000		
		847	10360		
		1000	13000		
		1050	13420		
		1100	14540		
		1150	15060		
		1200	15640		
		1250	15900		

The values of temperature are small relative to the electro-motive forces. This would result if the stem error applied is too small by an amount quite within the range of possible error, but it is more likely that the thermo-couple is here at a temperature above that of the air thermometer; in other words, that the environments are not identical. A reverse of this takes place on cooling; hence the use of a simple non-reentrant bulb for comparison is not at once permissible. It is necessary if the results are to be uniform and comparable, that both bulb and thermo-electric junction be not only contiguous, but be enveloped in some thick non-conducting substance. Such additional appliance is objectionable, since it interferes with quick and facile manipulation, and at high temperatures is fused into the glaze of the bulb in a way that endangers it. Mere contiguity of the junction and the bulb, even in case of a revolving muffle, is not a sufficient guaranty for the accuracy of the calibration results obtained.

Digression.—Before resolving to change the form of the bulb, I made another series of experiments, which have an ulterior interest, inasmuch as they are made with the soldered bulbs, glazed both within and without, which are described above, p. 175. It was also expedient, if not necessary, to change the method of measurement, and in the following results, Table 54, the constant-volume method is replaced by the constant-pressure method. The data are given in a way that will be fully explained in the next paragraph (p. 217), and it is here only necessary to refer to the time series of T, the temperature of the bulb, and of e_{20}, the corresponding electromotive force. Corresponding values of e_{20} and

T are collected in Table 55, and obtained as before by graphic interpolation. The results are inserted here because of the non-re-entrant form of bulb employed.

TABLE 54.—*Comparison of air thermometer and thermo-couple.*

In glazed bulb No. 2 $\left\{\begin{array}{l} v_0 = 282^{cc} \\ t = 20^\circ \end{array}\right.$					Thermo-couple No. 87.			
V_1	T_1	B_0	T	Time.	t_0	e_{20}	Time.	Gas-cock.
cc.	*°C.*	*cm.*	*°C.*	*hours.*	*°C.*	*microvolt.*	*hours.*	
147.0	24.3	76.46	333	1.12	22.4	3039	1.05	2
149.7	24.3	76.46	345	1.17	22.6	3534	1.22	2
154.3	24.3	76.46	366	1.28	22.8	3743	1.34	2
157.0	24.6	76.46	379	1.38	23.1	3906	1.48	2
160.4	24.8	76.46	396	1.55	23.6	4110	1.78	2
163.1	25.5	76.46	409	1.88	23.7	4104	1.92	2
163.4	25.4	76.46	411	1.98				
192.5	26.1	76.46	621	2.28	24.8	7160	2.33	3
196.0	26.2	76.46	655	2.37	24.9	7455	2.42	3
201.9	26.6	76.46	716	2.78	25.4	7926	2.67	3
202.5	26.7	76.46	722	2.84	25.8	8076	2.81	3
211.7	26.9	76.46	841	3.12	26.6	10270	3.17	3.5
216.0	27.0	76.46	907	3.33	26.8	10621	3.30	3.5
216.6	26.9	76.46	910	3.47	27.0	10748	3.42	3.5
217.4	27.1	76.46	931	3.67	27.4	10940	3.58	3.5
219.0	26.9	76.46	960	3.82	28.1	11602	3.87	3.7
220.7	26.8	76.46	994	3.98	28.3	11793	3.95	3.7
222.2	27.1	76.46	1019	4.13	28.4	12052	4.05	3.7
223.0	27.0	76.46	1036	4.25	28.6	12364	4.20	3.7
223.2	26.9	76.46	1041	4.40	28.6	12470	4.37	3.7
220.0	26.5	76.46	985	4.58	29.1	10480	4.65	Gas off.
215.0	26.0	76.46	903	4.68	29.3	9563	4.73	
210.0	25.8	76.46	828	4.78	29.3	8807	4.81	
205.3	25.5	76.46	767	4.87	29.3	8155	4.88	
200.2	25.3	76.46	707	4.97	29.4	7339	5.00	
189.8	25.0	76.46	602	5.20	29.1	6404	5.18	
180.8	25.2	76.53	528	5.42	29.0	5049	5.33	
170.0	25.2	76.53	452	5.68	28.8	5009	5.50	
160.2	25.1	76.53	396	5.93	28.7	4275	5.73	
154.8	25.0	76.53	369	6.05	28.6	3835	5.88	
145.3	24.8	76.53	325	6.30	28.6	3589	5.98	
140.4	24.8	76.53	307	6.42	28.6	3344	6.08	
129.8	24.0	76.53	267	6.68	28.4	2979	6.27	
124.9	23.7	76.53	251	6.80	28.2	2759	6.38	
					27.6	2325	6.65	

TABLE 55.—*T and* e_{20} *from Table* 54.

[Non-re-entrant inglazed bulb No. 2; thermo-couple No. 37.]

T	e_{20}	T	e_{20}	T	e_{20}
°C.	*microvolt.*	°C.	*microvolt.*	°C.	*microvolt.*
333	3240	907	10650	767	8270
345	3360	919	10800	707	7550
366	3640	931	11000	602	6320
379	3780	994	11860	528	5320
396	4000	1019	12220	452	4430
409	4100	1036	12400	396	3710
411	4110	1041	12600	369	3410
655	7300	903	10150	325	2940
716	8040	828	9100	307	2720
722	8100			267	2300

In the up-going series, in which observations were made only during periods of very constant temperature, the values of electro-motive force are normal in comparison with values of temperature. The boiling point of zinc, for instance, is fixed at 930°. In the down-going series thermo-electromotive force is too small, as usual. The effect, however, is possibly exaggerated by the great difficulty of making these bulbs absolutely tight. Nor is it possible to estimate the leak effect as a function of time, for the capillary canals change with temperature and even by accidental disturbances.

Difficulties such as are here described led me to the construction of the re-entrant form of bulb, in which, by a simple device, they are wholly obviated. This will be shown at length in the final section, which follows. I have purposely given a full series of data in Tables 50 to 55, in order to bring before the mind the extreme difficulty encountered in making comparisons between the thermo-couple and the air thermometer, when the conditions to be met are accuracy and expedition.

CONSTANT PRESSURE AIR THERMOMETRY—APPARATUS.

The above data were investigated in the rational endeavor to adapt Jolly's very convenient form of air thermometer to high-temperature measurements.[1] To do this I found it desirable to use low-pressure (<1 atmosphere) manometers, so that at high temperatures, when porcelain shows a tendency to become viscous, the pressures on the interior and on the exterior of the hot bulb may not differ by an amount sufficient to deform the bulb seriously. But while on the one hand this can never be perfectly accomplished, the difficulty of maintaining the air in the bulb and manometer at an invariable low pressure makes this instrument unusually liable to errors or accidents on the other. In the constant-pressure method of air thermometry, all hurtful excesses of pressure on the bulb

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[1] Weinhold, Erhardt, and Schertel tried it before (cf., p. 33, 34).

may be almost wholly excluded, the pressure chosen being, of course, that of the atmosphere. In this method, however, the volume of the bulb must be accurately known, a datum which is only of secondary importance in the constant-volume method.

Again, the above data are obtained with spherical bulbs of the non-re-entrant form. The difficulty experienced in obtaining a degree of satisfactory accordance in the various series of data is due to the fact that the environments are not identical. Hence in the following experiments the re-entrant form of bulb (Fig. 32) will be used, in which an identical exposure has been as nearly as possible realized. It will still be necessary to operate with bulbs not glazed internally. For final work bulbs of the re-entrant form, constructed in accordance with the Deville and Troost plan (Fig. 33), so as to be easily glazed internally, are available.

A very convenient and simple apparatus for constant-pressure air thermometry is given in Fig. 40, $\frac{1}{10}$ actual size. The details of construction are very similar to those shown in Fig. 30, and it is therefore only necessary to indicate the essential points of difference. In the present instrument the platinum capillary tube *A*, the further end of which communicates with the air-thermometer bulb, is soldered with resinous cement into the top of a long cylindrical tube, *B C*. The length of this tube is at least 150^{cm}; it is accurately graduated in cubic centimeters, and the total capacity is about 300^{cc}. In my apparatus the tube *B C* was closed below with a rubber cork, and this end then inserted with plaster of Paris into a suitable rest or foot. By removing the foot and the cork the tube admits of being cleaned, an operation which, for the case of imperfectly pure mercury, is sometimes necessary. Practically the tube is closed below, but it is provided at a short distance above its end with a horizontal tubulure, *D E*, to which a cloth-wrapped rubber hose, *E F G*, is attached. The upper end of *E F G* communicates by means of a three-way cock, *H*, with a large cylindrical vessel of mercury, *K L L*. The cock *H* has a lateral tubulure, *h*, through which mer-

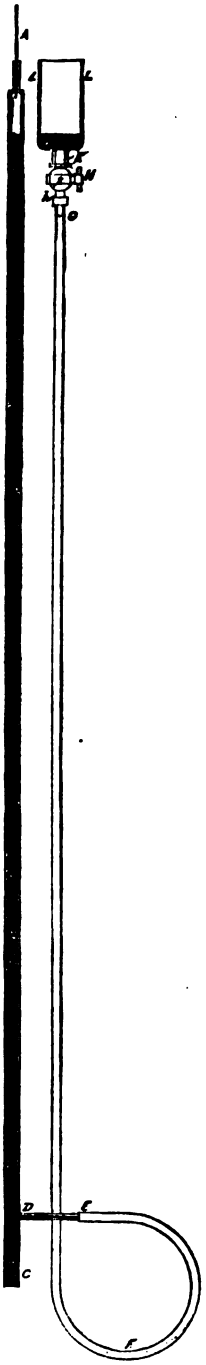

FIG. 40. Constant-pressure air-thermometer.

cury may be withdrawn either from the tube *B C* or from the reservoir *K L L*. The latter and the cock *H* may be unscrewed from the steel piece inserted into the hose at *G* in the manner shown in Fig. 30, above. This system is practically a U-tube, one of the arms of which may be varied in height or length at pleasure. For this purpose it is attached to the manometer stand, already described. (See frontispiece under *B*.) *B C* is fixed to one of the uprights with its weight mainly resting on the foot at *C*. The reservoir *K L L* and the cock *H* are fixed to the slide, which may be moved at pleasure up or down and clamped in any position on the second parallel upright of the manometer stand. The slide is conveniently provided with an ordinary micrometer screw, by which a finer adjustment is obtainable. Enough mercury is introduced to just fill the tube *B C* and leave a well-defined meniscus in the reservoir *K L L*. Moreover, the dimensions of *K L L* are such that when it occupies its lowest position, and the mercury is almost completely out of the tube *B C*, the reservoir may be about filled. Measurements are made with the cathetometer, which in this case, however, has no other purpose than to indicate identity in the level of the menisci in *B C* and *KLL*. The pressure is then that of the barometer, which may be conveniently suspended from the same stand. (See frontispiece.) Volumes are read off directly on the glass tube *B C*. Two sensitive thermometers at the lower and upper parts of this tube, respectively, show its temperature.

This is the form in which the apparatus was used. It will be remembered that the chief purpose of the present memoir is to test the availability of methods. Whenever it becomes desirable to investigate data of extreme accuracy, it is, of course, necessary to surround *B C* with a jacket of water, so that the temperature throughout its length may be kept rigorously constant. Again, the increment of volume, corresponding to a given increment of temperature, decreases in proportion as temperature itself increases. Hence, if it be desirable to measure high temperatures, a volume tube may expediently be chosen, of which the lower part is of smaller diameter than the upper part. Data for the construction of such tubes for any special purposes will be fully given in the tables below. Long capillary metallic tubes cool down the gas to atmospheric pressure before it enters the volumenometer tube *B C*.

CONSTANT-PRESSURE THERMOMETRY—METHOD OF COMPUTATION.

The general equation.—Equation (I), on page 189,

$$\Sigma\left[V\left(H\frac{1+\beta T}{1+\alpha T}-h\frac{1+\beta t}{1+\alpha t}\right)\right]=A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

applies here as it did in the case above. The former simplification consisted in so conducting the measurements that A=0. The present experiments accomplish a similar purpose by making $H=h$; for the value of A is easily found as

$$A=-HV_1\frac{1+\beta T_1}{1+\alpha T_1},$$

where V_1 is the excess of the volume of the gas at the high-temperature measurement T over that at the low-temperature measurement t, and where T_1 is the temperature of V_1. The older method therefore eliminates the volume factor; the present method eliminates the pressure factor.

If we expand equation (1) for the present case we find the following correlative variables:

$$\begin{array}{ccc} v & t & T \\ v' & t' & T' \\ v'' & t'' & T'' \\ \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot \\ \cdot\;\cdot & \cdot\;\cdot & \cdot\;\cdot \\ V_1 & - & T_1 \end{array}$$

where v is the volume of the bulb, v' the volume of the part of the stem along which temperature varies from T to t, v'' . . . the volumes of the remaining capillary stem and capillary tubes of nearly constant temperature, V_1, finally, the excess of volume of gas at the high-temperature measurement typified by T, over that of low-temperature measurement typified by t. Temperatures referring to the same volume are similarly accentuated. If for abbreviation

$$f(t)=\frac{1+\beta t}{1+\alpha t},$$

and

$$\Sigma=HS=\Sigma\frac{v'}{v}\Big[Hf(T')-hf(t')\Big],$$

then equation (1) leads to the following value of T:

$$T=\frac{H\left(1+\frac{V_1}{v}f(T_1)\right)-hf(t)+\Sigma}{\alpha\left(hf(t)-H\frac{V_1}{v}f(T_1)-\Sigma\right)-\beta H} \quad . \; . \; . \; . \; . \quad (2)$$

This equation is rigorously true; but it is unwieldy, and to be made practical must be simplified.

The equation simplified.—Equation (2) may be easily put into the form

$$T=\frac{H-hf(t)+H\frac{V_1}{v}f(T_1)+(1+\alpha T)\Sigma}{\alpha hf(t)-H\left(\alpha\frac{V_1}{v}f(T_1)-\beta\right)}, \quad . \; . \; . \; . \quad (3).$$

which for $H=h$, the condition underlying the present method, and for

$$M=f(t)-\frac{V_1}{v}f(T_1) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

an abbreviating expression, reduces to

$$T=\frac{1-M+\frac{S}{M}}{\alpha M-\beta} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

This is the form required. It is nearly rigorous, the approximations having been inserted in the corrective member $\frac{S}{m}$. It is perhaps interesting to annotate that the rigorous form (2), under the simplifying condition $H=h$ reduces to the unique expression

$$T=\frac{1+\frac{V_1}{v}f(T_1)-f(t)+S}{(\alpha-\beta)-\alpha\left(1+\frac{V_1}{v}f(T_1)-f(t)+S\right)}=\frac{P}{(\alpha-\beta)-\alpha P}$$

A few remarks on the practical method of using equation (5) are now in place. Equation (4) shows that t, the lower temperature at which measurement is made, furnishes the fiducial or fixed point of the air thermometer. t is obviously the temperature at which $V_1=0$ ***under the given barometric pressure*** b, *of the day* on which the measurements are made. Now, if at the barometric height B and at the temperature τ one observes $V_1=\nu$, then

$$f(t)=\frac{B}{b}\left(1+\frac{\nu}{\Sigma(v)}\right)f(\tau) \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

where $\Sigma(v)$ is the total volume of the bulb and capillary stems as far as the zero mark of graduation on the tube $B\,C$. Equation (6) follows at once from equation (1) in the general form given on page 189, if we impose $T=T'=T''= \ldots T_1$ and $t=t'=t'' \ldots$, the conditions given by the experiment. Equation (6) is therefore generally true. Usually b and B, t and τ differ but slightly and ν is nearly zero. Hence, having measured τ, B, ν, it is easy to find the value of t, which corresponds to the barometric height b of the day; and it is also easy to make allowance for any variation of barometric height occurring during the course of the experiment. These operations are simple and the corrections can mostly be made mentally.

Mere inspection of equations (4) (5) (6) shows that it is expedient to calculate a table for the function $f(t)=\frac{1+\beta t}{1+\alpha t}$, both for glass and for porcelain, once for all. Such a table in which t varies from 0° to 30°, in single degrees, will usually suffice. In this table, however, the data $\log f(t)$, which is more frequently in demand, must also be inserted for the same range of t.

If the re-entrant bulb be used, the mercury thermometer is conveniently inserted into the central tube while the bulb is in place in the revolving muffle. The stem of the mercury thermometer should be so long that the position of the thread may be seen. This furnishes τ of equation (6). It is frequently convenient to make this measurement for *unequal* heights of the columns of mercury in the two arms of the manometer. In this case B, of course, is the effective tension of the gas. The difference in height of the menisci is read off by the cathetometer.[1]

Volumetry of bulb.—Equations (4) and (5) contain the quantity V, or the volume of the bulb of the air thermometer at zero centigrade. This may, of course, be measured directly, before the high temperature work, by calibrating with water. If, however, a bulb non-glazed internally be used it is exceedingly difficult to dry it again thoroughly. Hence I have applied the volumetric method already utilized above in the case of stems. In the case of a manometer like the one described in Fig. 40 this method is applicable with great elegance, inasmuch as pressure can be varied over a large range and volumes read off with facility. In the following table an example of data obtained in this way is given. v_1 and p are corresponding values of the volume of the gas in the manometer tube BC (Fig. 40), and of the pressure. Measurements are made with the bulb and manometer in the air, and no thermal correction is applied:

TABLE 56.—*Volumetry of bulb.*

Date.	v_1	p	v_0
	cc.	*cm.*	*cc.*
Oct. 14	4.9	75.88	279.6
	122.2	53.73	
	4.8	75.93	280.1
	122.2	53.77	
Oct. 15	3.0	75.65	281.0
	120.2	53.55	
	30.0	75.66	280.9
	120.2	53.59	
	9.7	73.97	282.0
	120.8	53.56	
	6.5	74.82	281.3
	120.8	53.55	
	4.9	75.46	281.4
	120.9	53.70	
	7.4	74.93	279.9
	126.6	52.96	
Oct. 16	4.0	75.24	280.1
	126.0	52.64	
	4.0	75.22	281.3
	120.5	53.41	
	3.0	75.54	279.9
	120.5	53.38	
	3.0	75.53	281.3
		Mean v_0 =	280.73

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[1] Many operations may be simplified by using Landolt and Boernstein's physical tables; Berlin, 1883; cf. pp. 5 to 7.

The variations of v_0 here observed I was first inclined to attribute to the difficulty of defining the volume of a bulb, the interior of which is not glazed; but they are due to thermal disturbances. In order that the present method may be made to yield the best results the temperature of the bulb and of the manometer tube $B\ C$ (Fig. 40) must either be rigorously the same, or the respective temperatures must be known. For, if Σv be the volume of the bulb and capillary stems at the temperature t, and if V_1 and V_2 be the two volumes read off on the manometer tube $B\ C$ at the temperature T_1, and if H_1 and H_2 be the pressures or gas tensions which correspond, respectively, to V_1 and V_2, then

$$\frac{f(T_1)}{f(t)}\,\frac{H_1V_1-H_2V_2}{H_2-H_1}=\Sigma(v),$$

an expression in which if T_1 and t differ by as little as a few tenths of a degree the factor $f(T_1)/f(t)$ can no longer be considered negligible. It will be seen below that $\Sigma\ (v)$ must be measured with a degree of precision scarcely exceeding 0.02 per cent., i. e., to about 0.1^{cc} for the given capacity of bulb, if the *absolute* value of T is to be correct to one pro mille. But after many measurements, the further citation of which is here superfluous, I convinced myself that when due regard is paid to the temperature factor the accuracy in question is attainable. $f(T_1)\div f(t)$ is approximately $1+\alpha\,(t-T_1)$, in which form it may be easily applied.

Errors of the approximations.—It is necessary to discuss the corrective member of the equation (5).

$$T=\frac{1-M+\frac{S}{M}}{\alpha M-\beta}$$

viz, $\dfrac{\frac{S}{M}}{\alpha M-\beta}$, or as it may be written with sufficient accuracy, $\dfrac{S}{\alpha M^2}$.

For practice it is best to write for this the equivalent form $\dfrac{(1+\alpha T)^2S}{\alpha}$ and then to calculate a table from which, for each value of T, the value of this corrective function may be taken at once. It is usually sufficient to proceed as follows: The full form of the corrective function is

$$\left(\frac{1+\alpha T}{\alpha}\right)^2\Sigma\left\{\frac{v'}{v}\,[f(T')-f(t')]\right\}.$$

For those parts of the capillary stem whose temperatures are constant, $f(T'')$ and $f(t'')$ are practically identical. Hence the part of the stem along which temperature varies from the high value to that of the atmosphere alone enters into the consideration. It follows that the last expression may be written

$$\frac{(1+\alpha T)^2}{\alpha}\,\frac{v'}{v}\,[f(T')-f(t')].$$

Even this correction is small, and for 1,500° will not much exceed 5°. It is permissible therefore to put $T=2T'$ and to insert for t' a mean value. Table 57 is of the kind here referred to, and exhibits the values of $\frac{S}{\alpha M^2}$ for each value of T and for $t'=15°$; v'/v is found by measurement to be 0.00043.

TABLE 57.—*Errors of thermometer formulæ.*

T	$\frac{S}{\alpha M^2}$	T	$\frac{S}{\alpha M^2}$	T	$\frac{S}{\alpha M^2}$
°C		°C		°C	
100	− 0.0	600	− 0.6	1100	− 1.8
200	− 0.1	700	− 0.8	1200	− 2.2
300	− 0.2	800	− 1.0	1300	− 2.6
400	− 0.3	900	− 1.2	1400	− 2.9
500	− 0.4	1,000	− 1.5	1500	− 3.4

It will be seen by comparing this table, 57, with the similar one above (Table 45) for the constant-volume method that the errors here are very much smaller in magnitude. A result of this kind was to be anticipated, and the occurrence of small stem corrections, added to the fact that measurements are made in such a way that the tension of the gas inside the bulb need not exceed atmospheric pressure, is the salient advantage of the present method of high-temperature measurement over the constant-volume method.

Compensator.—In calculating the results of the last table no allowance is made for fissures or for the porosity of porcelain. Hence better results may be anticipated by using the compensator, though it always remains questionable whether the volumes of two nominally identical porcelain capillary stems are at all identical in fact. However, it is only the part of the compensator along which temperature varies from the high value T to that of the room that need be identical with the stem of the air thermometer. The remainder of the compensator may have any (capillary) volume, which need not be exactly the same as the volume of the capillary canals of the air thermometer. This appears fully from the formulæ below.

The theoretical introduction of the data of this apparatus is here quite simple; for it is seen that the quantity marked S in the equation, page 212, is the one immediately given by the compensator. It will be remembered that this apparatus is essentially a porcelain stem identical with the stem of the air thermometer, provided, however, with a manometer tube of much smaller caliber than the tube $B\,C$ of the manometer, page 210. Supposing therefore that the observations are made in the way already described for constant-pressure air thermometry, we have at once

$$S=\Sigma_{v}^{v'}\Big(f(T)-f(t')\Big)=-_{v}^{v_1}f(t_1)$$

where v_1 and t_1 have the same signification for the compensator that V_1 and T_1 have for the air thermometer. Inserting the expression

$$S=-\frac{v_1}{v}f(t_1)$$

into the equation (5) this becomes

$$T=\frac{1-M}{\alpha M-\beta}-\frac{v_1 f(t_1)}{\alpha M^2 v},$$

in which the correction is evaluated experimentally.

It will be shown below that the stem error is not of such serious importance in the constant-pressure method as it was in the constant-volume method; that the stem error rather falls below the other possible errors of measurement. Hence the use of the compensator is not to be as strenuously advised as it was above, and the correction derived merely from calibration and computation may be regarded satisfactory. This is, of course, a convenience, since it obviates the manipulation for the measurement of the two additional magnitudes v_1 and t_1. Such statements, however, must be made with caution, for it will appear that in the constant-pressure method, inasmuch as the volume of the bulb enters fundamentally into the computation, the real object of the compensator is to define the volume of the bulb. The true volume of the bulb, when the compensator is used, is its own volume plus the volume of the part of the capillary tube, the length of which is the difference of length of stem and of compensator.

CONSTANT-PRESSURE THERMOMETER—EXPERIMENTAL RESULTS.

Manipulation.—Before proceeding to the tabulation of final results it is expedient to refer to a few details of manipulation. On inserting the thermo-couple into the central tube of the air-thermometer bulb it is necessary to have the wires quite enveloped by the fire-clay insulators. This is done to avoid silicification. It is well to have the insulator within the air thermometer of smaller diameter than the straight tube which passes from the bulb to the outside of the furnace, for the porcelain glaze becomes viscous at high temperatures, and is liable to be absorbed by the insulator. Hence it is desirable to avoid such close contact as would be given by a tube filling the hole snugly. With due precautionary preventives of this kind silicification is nil. Of course, the thermo-couple must be kept in place while the furnace is cooling. If different thermo-couples are to be inserted this must be done while the furnace is heated or during the stages of rising temperature. With a well-dried bulb, symmetrically adjusted in the revolving muffle, the heating and cooling may be repeated almost indefinitely without breakage. Breakage is liable to occur when thermometers or muffles are exchanged. Wherever it is possible, it is well to avoid glass cocks.

Even when of best workmanship they are liable to leak after some usage. Moreover grease or vaseline is objectionable in consequence of the danger incurred of choking the capillary metal tubes.

Experimental data.—The data obtained in the experiments with the constant-pressure method are fully given in Tables 58 to 66. It is to be borne in mind that the results are obtained by a single observer, and that the chief object is to test the availability of methods rather than to reduce the results to extreme fineness. The manometer is in air, screened, however, from the furnace by a thick board and at some distance from it. v_0 denotes the volume of the bulb, and t is the fiducial temperature for the day. The bulbs are of the re-entrant form, not glazed internally. V_1 and T_1 are the volume and the temperature, respectively, of the air measured in the manometer tube $B\ C$ (Fig. 40). B_0 is the current barometric height. T is the temperature of the bulb at the time specified, all observations being made in time series.

Thermo-electric data are given on the same plan as above. t is the temperature of the cold junction, e_{20} the electro-motive force when the cold junction is 20° C. at the time specified. The figures of the last column refer to quantity of gas injected, as indicated by an arbitrary scale.

In Table 58 T_1 was read off by but a single thermometer, and T is therefore less accurate. In Table 59 the thermo-couple had to be taken out of the bulb during the stage of cooling, owing to an accident; the error thus produced is quite perceptible. The results in the remaining tables were obtained without accident.

The data as a whole (Tables 58 to 66) may be divided into two groups. In the first of these (Tables 58 to 61) the results are obtained with the re-entrant bulb No. 1, and the thermo-couple No. 37. These data are probably less accurate than the more complete series of the second group (Tables 62 to 66) in which the results are obtained with the re-entrant bulb No. 2 and the thermo-couples Nos. 37, 38, 39. The greater accuracy in the latter series of data is due to the fact that corrections are duly applied for the *permanent* contraction or dilatation of the porcelain bulb from measurements made after each heating. The method by which this may be done with extreme accuracy will be indicated below (p. 233).

Tables 58 to 61 contain the four series of observations classified under Group I.

TABLE 58.—*Comparison of air thermometer and thermo-couple. Series I. Method of constant pressure.*

Re-entrant bulb No. 1. $v_0=280°$. $t=19°.6$.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	t	e_{30}	Time.	Gas-cock.
cc.	*°C.*	*cm.*	*°C.*	*hours.*	*°C.*	*microvolt.*	*hours.*	
152.0	23.5	76.36	369	2.73	21.4	3454	2.70	2
157.0	23.9	76.36	394	2.92	21.7	3791	2.88	2
160.0	23.8	76.36	411	3.13	22.1	4076	3.17	2
161.0	23.9	76.36	416	3.30	22.4	4109	3.27	2
162.0	23.9	76.36	422	3.50	22.6	4189	3.45	2
203.2	24.9	76.36	781	3.98	23.1	8440	3.90	3
206.6	25.0	76.36	827	4.12	23.6	9226	4.03	3
207.2	25.0	76.36	836	4.25	23.8	9757	4.20	3
209.0	25.0	76.36	863	4.45	23.8	9981	4.33	3
209.0	25.0	76.36	863	4.50	24.0	10126	4.48	3

TABLE 59.—*Comparison of air thermometer and thermo-couple. Series II. Method of constant pressure.*

Re-entrant bulb No. 1. $v_0=280°$. $t=18°.6$.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	t	e_{30}	Time.	Gas-cock.
cc.	*°C.*	*cm.*	*°C.*	*hours.*	*°C.*	*microvolt.*	*hours.*	
191.5	25.7	76.01	607	1.09	23.6	6454	1.09	3
197.2	26.0	76.01	661	1.28	23.6	7152	1.20	3
203.7	26.8	76.01	728	1.73	24.6	7857	1.33	3
203.5	27.0	76.01	724	1.78	24.9	8276	1.70	3
203.4	27.1	76.01	722	1.83	25.4	8280	1.75	3
					25.6	8234	1.83	3
209.0	27.4	75.96	788	2.03	26.1	9404	2.07	3.5
211.2	27.5	75.96	818	2.18	26.6	9699	2.22	3.5
211.6	2707	75.96	822	2.35	26.6	9743	2.30	3.5
218.4	28.1	75.96	923	2.60	27.6	11204	2.58	3.7
219.0	28.2	75.96	932	2.77	27.6	11318	2.68	3.7
219.0	28.4	75.96	928	2.92	28.1	11319	2.80	3.7
					28.6	11354	3.00	3.7
210.5	27.9	75.95	803	3.20	29.4	8961	3.25	Gas off.
205.1	27.6	75.95	737	3.30	29.1	8040	3.35	
201.0	27.4	75.95	690	3.43	29.3	7175	3.48	
190.0	27.1	75.95	583	3.63	29.4	6122	3.68	
180.8	26.8	75.95	511	3.87	29.4	5179	3.92	
167.5	26.4	75.95	425	4.17	29.4	4234	4.20	
138.0	25.5	75.95	289	4.92	28.6	2574	4.98	
132.9	25.3	75.95	270	5.05	28.6	2528	5.00	

TABLE 60.—*Comparison of air thermometer and thermo-couple. Series III. Method of constant pressure.*

Re-entrant bulb No. 1. v_0 = 280. t = 13.8°.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	t	e_{30}	Time.	Gas-cock.
cc.	°*C.*	*cm.*	°*C.*	*hours.*	°*C.*	*microvolt.*	*hours.*	
150.0	24.3	74.96	322	1.17	22.4	2826	1.15	2
164.6	24.7	74.96	390	1.33	22.6	3543	1.25	2
172.5	25.1	74.96	434	1.62	23.1	4302	1.55	2
173.5	25.2	74.96	439	1.67	23.4	4445	1.65	2
176.4	25.5	74.96	456	1.95	23.6	4690	1.87	2
176.1	25.5	74.96	455	2.03	23.8	4673	2.00	2
198.7	25.7	74.98	633	2.92	25.6	6654	2.87	3
202.4	25.1	74.98	671	3.00	25.8	7474	2.97	3
205.5	25.8	74.98	704	3.15	26.1	8117	3.18	3
206.0	26.0	74.98	709	3.22	26.3	8278	3.33	3
207.0	26.0	74.98	720	3.37	......	....	....	......
215.4	26.2	75.06	840	3.58	26.6	9382	3.55	3.5
218.8	26.3	75.06	891	3.73	26.8	10209	3.63	3.5
220.5	26.4	75.06	918	3.98	27.2	11038	3.92	3.5
221.1	26.5	75.06	928	4.12	27.6	11157	4.03	3.5
223.3	26.7	75.09	958	4.28	27.8	11632	4.24	3.7
224.3	27.0	75.09	972	4.35	27.8	11952	4.32	3.7
225.3	27.0	75.09	991	4.49	28.2	12290	4.46	3.7
225.5	27.0	75.09	994	4.62	28.4	12328	4.57	3.7
225.5	27.1	75.09	994	4.67	28.6	12363	4.63	3.7
222.5	26.9	75.12	943	4.83	28.6	12288	4.77	Gas off.
204.6	25.8	75.12	700	5.19	28.9	9515	5.00	
195.5	25.9	75.12	606	5.41	29.0	7691	5.23	
183.8	26.0	75.12	509	5.70	29.1	0436	5.45	
175.7	25.8	75.12	455	5.88	29.1	5660	5.63	
160.5	25.5	75.12	370	6.27	29.1	5126	5.77	
150.9	25.6	75.12	325	6.52	28.8	3779	6.22	
147.8	25.6	75.12	319	6.61	28.6	3573	6.32	
144.6	25.5	75.12	300	6.68	28.6	3043	6.57	
					28.6	2795	6.70	

Table 61.—*Comparison of air thermometer and thermo-couple. Series IV. Method of constant pressure.*

Re-entrant bulb No. 1. $v_0=280$. $t=15.7°$.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	t	e_m	Time.	Gas-cock.
cc.	*°C.*	*cm.*	*°C.*	*hours.*	*°C.*	*microvolt.*	*hours.*	
139.2	23.5	75.57	288	1.20	21.6	2480	1.18	2
149.8	23.6	75.57	330	1.30	21.6	2952	1.27	2
157.0	24.0	75.57	364	1.48	21.8	3376	1.42	2
158.6	24.0	75.57	372	1.55	22.0	3579	1.52	2
161.6	24.1	75.57	387	1.75	22.4	3781	1.68	2
162.1	24.1	75. 7	390	1.82	22.6	3836	1.77	2
173.5	24.5	75.55	455	2.02	23.0	4295	1.97	2.5
179.4	24.7	75.55	494	2.12	23.2	4961	2.08	2.5
184.5	24.7	75.55	532	2.28	23.6	5602	2.27	2.5
186.0	24.8	75.55	543	2.43	23.7	5729	2.35	2.5
194.8	24.9	75.58	616	2.62	24.4	6418	2.57	2.7
197.0	25.1	75.58	641	2.68	24.6	7386	2.73	2.7
202.0	25.2	75.58	693	2.97	24.8	7783	2.90	2.7
203.0	25.3	75.58	704	3.07	25.1	8001	3.02	2.7
208.5	25.5	75.59	770	3.32	25.6	8761	3.27	3.0
210.8	25.6	75.59	801	3.47	25.8	9277	3.40	3.0
212.4	25.9	75.59	819	3.67	26.1	9691	3.62	3.0
215.2	26.0	75.61	861	3.87	26.6	10193	3.83	3.3
216.4	26.2	75.61	879	3.98	26.7	10490	3.93	3.3
218.8	26.4	75.61	914	4.13	27.1	11023	4.10	3.5
219.7	26.4	75.61	930	4.22	27.2	11366	4.18	3.5
220.9	26.5	75.61	950	4.38	27.4	11675	4.32	3.5
221.2	26.5	75.61	956	4.48	27.6	11803	4.43	3.5
221.5	26.9	75.61	957	4.70	27.1	11869	4.67	3.5
215.7	26.4	75.68	868	4.84	28.2	11589	4.76	Gas off.
210.1	26.1	75.68	790	4.97	28.4	9998	4.90	
205.1	25.8	75.68	729	5.07	28.5	8801	5.02	
200.1	25.4	75.68	675	5.17	28.6	8146	5.10	
194.0	25.5	75.68	621	5.28	28.6	7329	5.22	
190.0	25.4	75.68	577	5.40	28.6	6108	5.45	
184.4	25.5	75.73	525	5.55	28.6	5501	5.59	
180.0	25.5	75.73	500	5.65	28.6	5003	5.73	
163.8	24.2	75.73	402	6.03	28.4	3826	6.12	
155.2	23.9	75.73	359	6.25	28.2	3400	6.28	

Tables 62 to 66, exhibit the five series of observations classified as Group II. The last of these series (No. V) contains data for the measurement of the coefficient of expansion of the porcelain bulb. The method by which such data may be utilized is explained below on page 236.

TABLE 62.—*Comparison of air thermometer and thermo-couple. Series 1. Method of constant pressure.*

Re-entrant bulb No. 2. $v_0=286$. $t=16°$.					Thermo-couples Nos. 37, 39.			
V_1	T_1	B_0	T	Time.	No.	t	e_{20}	Time.
cc.	*°C.*	*cm.*	*°C.*	*hours.*		*°C.*	*microvolt.*	*hours.*
154.5	21.6	77.17	359	1.15	37	20.0	3521	1.22
157.4	21.7	77.17	373	1.28	37	20.1	3642	1.32
158.8	22.0	77.17	379	1.38	37	20.6	3747	1.43
160.1	22.2	77.17	385	1.52	37	20.8	3780	1.57
161.8	22.5	77.17	393	1.85	39	21.1	3837	1.80
162.3	22.6	77.17	396	1.97	39	21.2	3872	1.90
202.9	23.8	77.13	703	2.52	39	22.6	7742	2.42
205.0	24.4	77.13	733	2.80	39	22.8	8118	2.58
206.2	25.0	77.13	744	2.95	39	23.4	8408	2.88
208.0	26.0	77.13	758	3.23	37	24.6	8791	3.37
208.7	26.5	77.13	762	3.50	37	25.1	8795	3.55
208.9	26.6	77.13	763	3.63	37	25.6	8799	3.68
216.0	26.5	77.14	866	3.90	37	26.4	10644	3.98
219.2	27.1	77.14	910	4.07	37	26.6	11000	4.13
220.2	27.1	77.14	928	4.19	37	27.0	11140	4.23
220.8	27.1	77.14	938	4.57	39	27.7	11088	4.60
220.5	27.2	77.14	931	4.65	39	27.9	11063	4.67
220.4	27.4	77.14	927	4.75	......	......	......	......
223.8	28.8	77.16	972	5.32	39	28.8	12125	5.22
224.7	28.5	77.16	991	5.50	39	29.1	12113	5.40
225.8	28.1	77.16	1019	5.65	39	29.5	12476	5.62
223.3	28.7	77.16	963	6.10	37	30.2	11830	6.05
222.6	28.7	77.16	949	6.21	37	30.4	11552	6.17
222.2	28.1	77.18	952	6.30	37	30.6	11400	6.25
215.2	27.7	77.18	842	6.63	37	30.6	11057	6.51
210.4	27.3	77.18	779	6.73	37	30.6	9204	6.70
205.9	27.2	77.18	724	6.82	37	30.6	8500	6.77
200.5	27.0	77.18	665	6.93	37	30.8	7896	6.86
194.4	26.8	77.18	600	7.08	37	30.8	7131	6.98
189.9	26.7	77.19	567	7.18	37	30.7	6319	7.13
185.0	26.5	77.19	529	7.30	37	30.6	5821	7.24
180.0	26.4	77.19	493	7.43	37	30.5	5308	7.35
175.2	26.4	77.19	460	7.54	37	30.4	5032	7.44
170.1	26.1	77.19	430	7.67	37	30.1	4138	7.73
165.2	26.0	77.19	402	7.80	37	30.0	3853	7.83
159.8	25.7	77.19	375	7.92	37	29.8	3560	7.96
154.7	25.7	77.19	351	8.04	37	29.8	3291	8.08
150.1	25.7	77.23	330	8.17				

TABLE 63.—*Comparison of air thermometer and thermo-couple. Series II. Method of constant pressure.*

Re-entrant bulb No. 2. $v_0 = 286$. $t = 14°.7$.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	No.	t	e_{30}	Time.
cc.	°*C.*	*cm.*	°*C.*	*hours.*	.	°*C.*	*microvolt.*	*hours.*
223.7	24.7	77.14	1021	2.18	37	22.1	12654	2.22
225.4	25.2	77.14	1048	2.30	37	22.6	13095	2.38
227.0	25.6	77.14	1075	2.47	37	23.6	13341	2.53
227.5	25.9	77.14	1080	2.60	37	23.8	13372	2.63
224.8	25.8	77.14	1027	2.77	37	24.6	11592	2.82
219.8	25.7	77.14	934	2.85	37	24.8	10479	2.92
214.9	25.3	77.14	858	2.95	37	25.1	9560	3.00
210.1	25.3	77.14	789	3.04	37	25.5	8793	3.08
205.2	25.3	77.14	726	3.15	37	25.8	7997	3.18
200.3	25.2	77.14	671	3.25	37	25.8	7326	3.28
195.0	25.1	77.13	618	3.38	37	26.2	6662	3.40
190.2	24.8	77.13	575	3.49	37	26.4	6106	3.52
185.1	24.7	77.13	534	3.62	37	26.6	5444	3.67
180.4	24.6	77.13	499	3.73	37	26.5	5067	3.77
175.0	24.4	77.13	462	3.85	37	26.6	4643	3.90
170.0	23.8	77.14	433	3.97				

TABLE 64.—*Comparison of air thermometer and thermo-couple. Series III. Method of constant pressure.*

Re-entrant bulb No. 2. $v_0=279$. $t=13°$.					Thermo-couple No. 39.			
V_1	T_1	B_0	T	Time.	t	e_{30}	Time.	Gas-cock.
cc.	°*C.*	*cm.*	°*C.*	*hours.*	°*C.*	*microvolt.*	*hours.*	
223.5	23.9	76.62	989	2.58	21.4	11544	2.48	4
224.9	23.8	76.62	1019	2.73	21.7	12198	2.66	4
225.5	24.0	76.62	1028	2.83	22.2	12509	2.78	4
226.7	24.1	76.62	1051	3.02	22.4	12710	2.90	4
227.0	24.3	76.62	1055	3.12	22.8	12909	3.07	4
224.8	23.8	76.60	1017	3.27	24.1	11567	3.33	Gas off.
220.0	23.6	76.60	929	3.37	24.1	10453	3.42	
214.8	23.4	76.60	846	3.47	24.2	9536	3.50	
209.8	23.2	76.60	778	3.56	24.6	8769	3.57	
205.2	23.0	76.60	721	3.65	24.8	7454	3.75	
200.0	22.8	76.60	664	3.77	24.9	7067	3.82	
195.2	22.7	76.60	616	3.87	25.1	6443	3.93	
190.4	22.6	76.60	573	3.99	25.2	5920	4.05	
184.8	22.4	76.60	527	4.13	25.3	5343	4.18	
180.4	22.3	76.60	494	4.23	25.2	4977	4.28	
175.1	22.5	76.60	458	4.37	25.1	4564	4.41	
170.0	22.4	76.60	426	4.48	25.1	4214	4.52	
165.2	22.4	76.62	403	4.60				

TABLE 65.—*Comparison of air thermometer and thermo-couple. Series IV. Method of constant pressure.*

Re-entrant bulb No. 2. $v_0 = 279$. $t = 10°.4$.					Thermo-couple No. 37.			
V_1	T_1	B_0	T	Time.	t	e_{20}	Time.	Gas-cock.
cc.	°*C.*	*cm.*	°*C.*	*hours.*	°*C.*	*microvolt.*	*hours.*	
227.8	27.2	76.01	976	2.37	25.6	12027	2.43	4
228.5	27.3	76.01	990	2.47	25.8	12096	2.50	4
228.6	27.4	76.01	990	2.53	25.9	12133	2.57	4
229.0	27.6	76.01	995	2.58	26.0	12168	2.60	4
225.0	27.5	76.01	923	2.76	26.3	11586	2.73	Gas off.
220.2	27.4	76.00	847	2.85	26.6	10374	2.82	
214.8	27.3	76.00	773	2.95	27.0	9560	2.89	
210.0	27.2	76.00	714	3.05	27.2	8791	2.97	
204.9	27.1	76.00	659	3.15	27.4	7845	3.08	
199.8	27.0	76.00	609	3.27	27.6	7091	3.20	
195.2	26.9	76.00	569	3.38	27.8	6467	3.32	
190.5	26.8	76.01	531	3.50	28.1	5945	3.43	
185.0	26.7	76.01	490	3.63	28.2	5503	3.53	
180.2	26.6	76.01	459	3.75	28.4	5040	3.66	
174.8	26.4	76.01	427	3.87	28.4	4593	3.79	
170.3	26.3	75.98	402	3.98	28.4	4163	3.93	

TABLE 66.—*Comparison of air thermometer and therme-couple. Series V. Method of constant pressure.*

Re-entrant bulb No. 2. $v_0 = 279$. $t = 10°$.					Thermo-couple No. 38.			
V_1	T_1	B_t	T	Time.	t	e_{20}	Time.	Gas-cock.
cc.	°*C.*	*cm.*	°*C.*	*hours.*	°*C.*	*microvolt.*	*hours.*	
182.8	18.8	76.25	512	11.26	16.6	5093	11.17	2.5
184.8	18.8	76.25	526	11.34	17.0	5490	11.30	2.5
189.9	19.3	76.20	565	11.67	17.4	5854	11.51	2.5
190.5	19.4	76.20	568	11.75	18.6	6040	12.07	2.5
105.6	20.1	107.64	....	11.88	19.6	6132	12.48	2.5
190.0	19.7	76.15	560	12.05	20.4	8083	12.77	3.0
105.8	20.4	107.57	....	12.27	20.8	8638	1.01	3.0
191.2	20.3	76.12	567	12.42	21.2	8781	1.19	3.0
208.0	21.1	76.06	734	12.88	21.6	8856	1.31	3.0
209.0	21.5	76.06	742	12.95	22.1	9064	1.61	3.0
211.0	22.0	76.06	760	1.28	22.6	9012	1.83	3.0
212.8	22.5	....	774	1.82	23.6	11561	2.37	3.7
225.4	23.5	75.92	958	2.42	23.8	11880	2.50	3.7
226.5	23.6	....	978	2.57	23.8	11998	2.62	3.7
121.4	24.6	118.50	....	2.83	24.6	12203	2.87	3.7
228.2	24.2	118.50	1002	2.97	24.8	12328	3.00	3.7
125.2	25.1	116.72	....	3.17	25.1	12366	3.22	3.7
228.9	24.3	75.85	1006	3.27	25.4	12553	3.38	3.7

TABLE 66.—*Comparison of air thermometer and thermo-couple. Series V. Method of constant pressure*—Continued.

Re-entrant bulb No. 2. $v_0=279$. $t=10°$.					Thermo-couple No. 38.			
V_1	T_1	B_t	T	Time.	T	e_{20}	Time.	Gas cock.
cc.	°*C.*	*cm.*	°*C*	*hours.*	°*C.*	*microvolt.*	*hours.*	
225.0	24.3	75.54	935	3.53	25.4	12439	3.45	Gas off.
219.6	23.7	75.54	852	3.64	25.6	10991	3.57	
215.1	23.5	75.54	790	3.73	25.8	9893	3.66	
209.6	23.3	75.54	722	3.84	25.8	8991	3.75	
205.0	23.0	75.56	671	3.94	25.8	8126	3.86	
200.0	22.7	75.56	622	4.06	25.8	7309	3.98	
195.1	22.3	75.56	579	4.18	25.8	6642	4.10	
190.1	22.0	75.56	539	4.31	25.6	6085	4.23	
184.9	21.6	75.57	501	4.42	25.6	5480	4.37	
179.9	21.2	75.57	467	4.53	25.4	5096	4.47	
175.0	21.2	75.57	436	4.66	25.3	4763	4.56	
170.0	21.5	75.54	405	4.78	25.2	4382	4.68	
					25.1	4134	4.77	

The results of these tables were constructed graphically by representing on the same sheet T and e_{20}, respectively, as functions of time. For the pairs of curves thus obtained it is easy to select data for the construction of e_{20} as a function of T with a degree of accuracy consistent with the accuracy of measurement. Such data are enumerated in Tables 67 to 70, which correspond, respectively, to the four tables just described.

It is perhaps well to remark that generally the interpolations are made linearly. This involves less assumption and less work than other graphic methods, and the points are sufficiently near together to make it available.

Tables 67 to 70 correspond to the data of Group I, Tables 58 to 61.

TABLE 67.—*Corresponding to Table* 58.

Series I.—Re-entrant bulb No. 1.					
No.	T	e_{20}	No.	T	e_{20}
37	370	3530	37	780	8950
37	390	3810	37	800	9200
87	400	3940	37	820	9470
37	410	4050	37	840	9770
37	420	4170	37	850	9940
			37	860	10100

TABLE 68.—*Corresponding to Table* 59.

Series II.—Re-entrant bulb No. 1.

No.	T	e_{20}	No.	T	e_{20}	No.	T	e_{20}
37	610	6520	37	824	9740	37	600	6430
37	640	7160	37	920	11200	37	550	5820
37	667	7700	37	930	11300	37	500	5220
37	720	8290	37	933	11330	37	450	4640
37	727	8270	37	750	8580	37	400	4030
37	800	9410	37	700	7820	37	350	3420
37	820	9660	37	650	7100	37	300	2800

TABLE 69.—*Corresponding to Table* 60.

Series III.—Re-entrant bulb No. 1.

No.	T	e_{20}	No.	T	e_{20}	No.	T	e_{20}
37	330	3120	37	860	10200	37	800	9320
37	360	3500	37	880	10500	37	750	8640
37	425	4300	37	900	10800	37	700	7960
37	440	4460	37	920	11150	37	650	7250
37	453	4660	37	960	11850	37	600	6550
37	630	7100	37	980	12170	37	550	5860
37	660	7500	37	990	12340	37	500	5280
37	690	7860	37	994	12370	37	450	4700
37	710	8160	37	950	11580	37	400	4080
37	718	8270	37	900	10760	37	350	3420
37	840	9840	37	850	10040	37	300	2840

TABLE 70.—*Corresponding to Table* 61.

Series IV.—Re-entrant bulb No. 1.

No.	T	e_{20}	No.	T	e_{20}	No.	T	e_{20}
37	330	3010	37	700	8050	37	850	10320
37	350	3330	37	770	9000	37	800	9470
37	370	3620	37	790	9280	37	750	8670
37	390	3850	37	810	9550	37	700	7970
37	480	4960	37	815	9650	37	650	7340
37	500	5220	37	870	10520	37	600	6660
37	520	5470	37	890	10860	37	550	5970
37	540	5740	37	910	11170	37	500	5280
37	640	7200	37	930	11470	37	450	4650
37	660	7430	37	950	11760	37	400	4020
37	680	7680	37	957	11860	37	350	3430

The series of Tables 71 to 75 correspond to the data of Group II, Tables 62 to 66.

TABLE 71.—*Corresponding to Table 62.*

Series I.								
No.	e_{30}	T	No.	e_{30}	T	No.	e_{30}	T
	microvolt.	°C.		*microvolt.*	°C.		*microvolt.*	°C.
37	3410	359	37	10640	895	37	....	842
37	3570	373	37	10850	910	37	8900	779
37	3700	379	37	11080	928	37	8160	724
37	3770	385	39	11090	938	37	7450	665
39	3850	393	39	11070	931	37	6580	606
39	3900	396	39	11050	927	37	6080	567
39	7970	703	39	12120	972	37	5590	529
39	8340	733	39	12290	991	37	5060	493
39	8470	744	39	12440	1019	37	4730	460
37	8670	758	37	11720	963	37	4330	430
37	8800	762	37	11470	949	37	3940	402
37	8800	763	37	11400	952	37	3660	375
						37	3370	351
						37	....	330

TABLE 72.—*Corresponding to Tables 63, 64, 65.*

Series II.			Series III.			Series IV.		
No.	e_{30}	T	No.	e_{30}	T	No.	e_{30}	T
	microvolt.	°C.		*microvolt.*	°C.		*microvolt.*	°C.
37	12650	1030	39	11900	989	37	12040	985
37	12870	1048	39	12370	1019	37	12060	990
37	13250	1075	39	12590	1028	37	12110	990
37	13360	1080	39	12850	1051	37	12140	995
37	11250	934	39	12910	1054	37	11120	923
37	10150	858	39	11570	965	37	10040	847
37	9170	789	39	11080	929	37	8970	773
37	8240	726	39	9880	846	37	8110	714
37	7540	671	39	8880	778	37	7410	659
37	6780	618	39	8180	721	37	6740	609
37	6250	575	39	7350	664	37	6180	569
37	5660	534	39	6780	616	37	5640	531
37	5220	499	39	6170	573	37	5140	490
37	4820	462	39	5550	527	37	4740	459
37	....	433	39	5150	494	37	4350	427
			39	4700	458	37	4140	413
			39	4350	426			
			39	....	403			

TABLE 75.—*Corresponding to Table 66.*

Series V.								
No.	e_{20}	T	No.	e_{20}	T	No.	e_{20}	T
	microvolt.	°*C.*		*microvolt.*	°*C.*		*microvolt.*	°*C.*
38	5370	512	38	9030	774	38	7580	671
38	5560	526	38	11700	958	38	6860	622
38	5900	565	38	11950	978	38	6300	579
38	5930	568	38	12300	1002	38	5740	539
38	6030	560	38	12430	1006	38	5290	501
38	6100	567	38	11470	935	38	4880	467
38	8310	734	38	10130	852	38	4450	436
38	8500	742	38	9190	790	38	4100	405
38	8850	760	38	8270	722			

Graphic digests.—The results of these four tables may be platted graphically by making e_{20} a function of T. This is done in Figs. 41 and 42, which may be said to be the final result of the calibration problem in hand. Fig. 41 contains the data of Group I, Fig. 42 the data of Group II. In Fig. 41 numerals inserted show the series to which the point of observation refers. If temperature be increasing (heating) the numeral is placed above the point; if temperature be decreasing (cooling) the numeral is below the point. In Fig. 42 similar distinctions are carried out by caudal dashes. For increasing temperature these point upward or to the right; for decreasing temperature downward or to the left.

CONSTANT-PRESSURE THERMOMETER—DISCUSSION.

Errors of measurement in general.—The discussion of the data, Tables 67 to 75, may expediently be introduced by an analysis of the effect of errors. The divers quantities, which enter saliently into the equation, derived for constant-pressure air thermometry, are here

$$t,\ T_1,\ \frac{V_1}{v},\ \frac{v'}{v},\ \frac{H}{h},\ \alpha,\ \beta,\ .$$

to which may be added M and S. As above, the degree of absolute accuracy with which they are to be measured in order that the effect on T may not exceed 1 : 1000, follows from the equation

$$\delta x = \frac{dx}{dT}\ \frac{T}{1000}$$

where x typifies any one of the quantities enumerated. From this follow the subjoined special equations, all of which are approximate, and put in such forms as will best facilitate the computation:

$$\delta M = -\frac{\alpha}{1000}\,\frac{T}{(1+\alpha T)^2}$$

$$\delta S=\frac{\alpha}{1000}\frac{T}{(1+\alpha T)^2}=-\delta M$$

$$\delta t=\frac{(1+\alpha t)^2}{1000}\frac{T}{(1+\alpha T)^2}=-\frac{(1+\alpha t)^2}{\alpha}\delta M$$

$$\delta T_1=-\frac{(1+\alpha T_1)^2}{1000}\frac{T}{\frac{V_1}{v}(1+\alpha T)^2}=+\frac{v(1+\alpha T_1)^2}{\alpha}\frac{\delta M}{V_1}$$

$$\delta\frac{V_1}{v}=\frac{\alpha}{1000\,f(T_1)}\frac{T}{(1+\alpha T)^2}=-\frac{1}{f(T_1)}\delta M$$

$$\delta\frac{v'}{v}=\frac{\alpha}{1000\,[f(T')-f(t')]}\frac{T}{(1+\alpha T)^2}=-\frac{1}{[f(T')-f(t')]}\delta M$$

$$\delta v=-\frac{\alpha v^2}{1000 f(T_1)}\frac{T}{V_1(1+\alpha T)^2}=+\frac{v^2}{f(T_1)}\frac{\delta M}{V_1}$$

$$\delta\alpha=\frac{\alpha}{1000}$$

$$\delta\beta=\frac{\alpha}{1000}\frac{1}{1+\alpha T}$$

$$\delta\left(\frac{H}{h}\right)=\frac{\alpha}{1000\,f(t)}\frac{\left(f(t)-\frac{H}{h}\frac{V_1}{v}f(T_1)\right)^2}{f(t)}T=\frac{\alpha f(t)}{1000}\left(1-\frac{V_1}{v}\frac{f(T_1)}{f(t)}\right)^2 T$$

These forms have a more general importance, inasmuch as they show what correction is to be applied to T to compensate for unavoidable or current errors of any of the special quantities to which the formulæ refer. Such errors, for instance, are the permanent changes of volume of the porcelain bulb in successive heatings, and due to the vitrification of porcelain. The correction to be applied is

$$\delta T=-\frac{f(T_1)}{\alpha v^2}V_1(1+\alpha T)^2\delta v.$$

It is well to remark that $\frac{V_1}{v}$ in the above equations has approximately the value

$$\frac{V_1}{v}=1-\frac{1}{f(T_1)(1+\alpha T)},$$

since for the present purposes t and T_1 may be supposed identical.

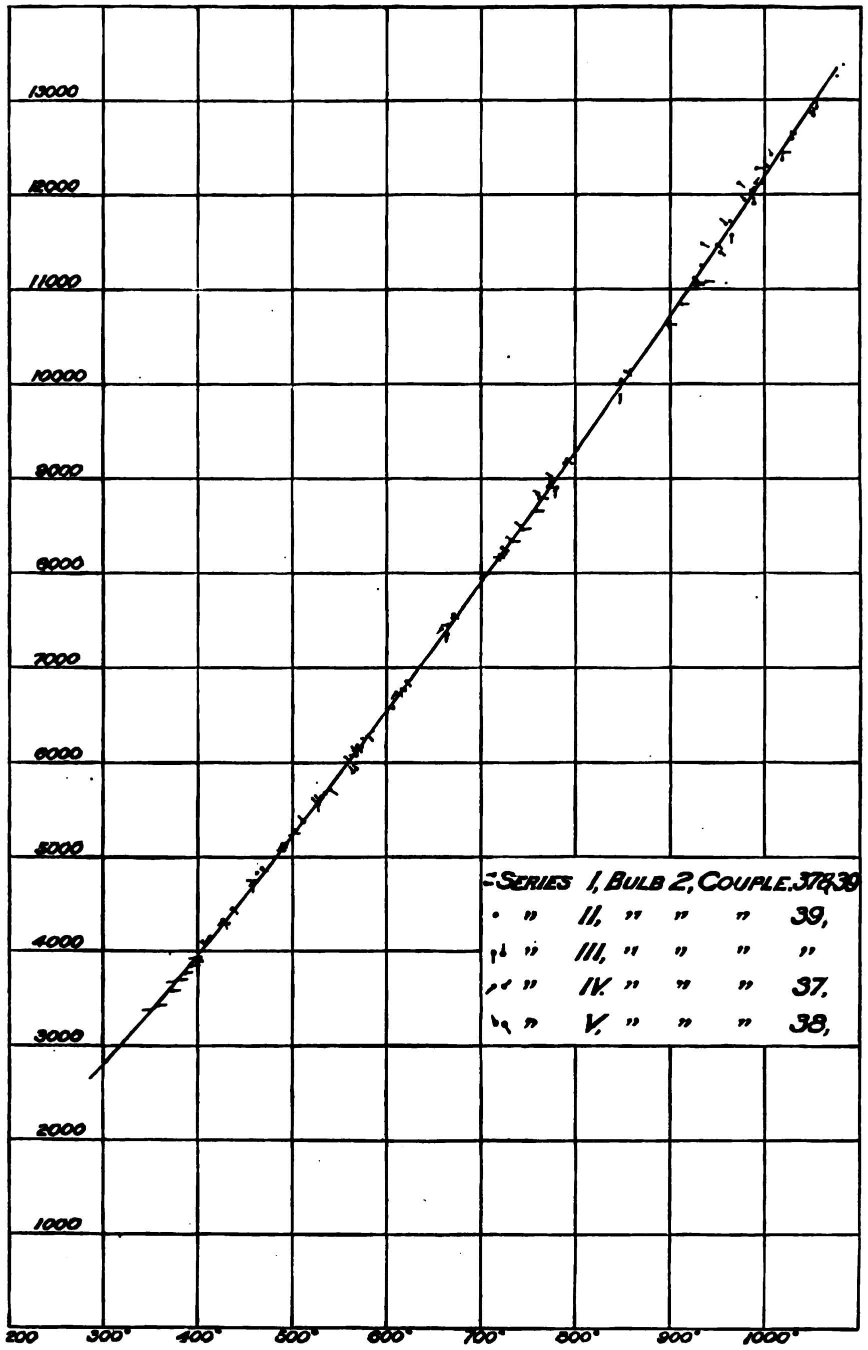

FIG. 42.—Chart showing the variation of thermo-electromotive force (microvolts) with temperature.

$\delta(H/h)$ must be derived from the general equation, which, after differentiation, is simplified by inserting $H=h$.

If into these equations we introduce mean values, such as $t=20^\circ$, $T_1=20^\circ$, $\alpha=0.00367$, $\beta=0.000017$; if, moreover, we insert for $\frac{V_1}{v}$ the values which may be taken from Tables 58 to 66, above, then the said equations lead to the following tabular comparison. It is expedient in addition to the absolute values of the divers errors δt, δT_1, δV_1, $\delta v'$, δv, $\delta\alpha$, $\delta\beta$, δH, δM, δS, which individually influence the result by 1: 1000, to give also the relative values of some of these quantities, or again the error of the ratios, viz:

$$\frac{\delta\beta}{\beta},\ \delta\left(\frac{V_1}{v}\right),\ \delta\left(\frac{v'}{v}\right),\ \delta\left(\frac{H}{h}\right),\ \delta(M)/M, \text{and } \delta(S)/S.$$

TABLE 76.—*Comparison of divers errors which affect the result one pro mille.*

T	δt	δT_1	δV_1	$\delta v'$	$\delta\beta\times10^6$	δH	$\delta M\times10^6$	$\delta S\times10^6$
°*C.*	°*C.*	°*C.*	*cc.*	*cc.*		*cm.*		
100	0. 06	—0. 29	0. 059	—0. 632	2. 7	0. 016	—197	197
500	0. 07	—0. 12	0. 069	—0. 155	1. 3	0. 019	—228	228
1000	0. 05	—0. 07	0. 051	—0. 081	0. 8	0. 014	—168	168
1500	0 04	—0. 05	0. 039	—0. 055	0. 6	0. 011	—130	130

δv	$\delta\beta/\beta$	$\delta\left(\frac{V_1}{v}\right)\times10^6$	$\delta\left(\frac{v'}{v}\right)\times10^3$	$\delta M/M\times10^6$	$\delta S/S$	$\delta\left(\frac{H}{h}\right)\times10^6$	V_1	T
cc.							*cc.*	°*C.*
—0. 276	0. 17	211	—2. 26	—268	—5. 27	211	59. 9	100
—0. 111	0. 08	245	—0. 56	—647	—1. 30	245	173. 9	500
—0. 066	0. 05	180	—0. 29	—736	—0. 68	183	215. 3	1000
—0. 047	0. 04	140	—0. 20	—846	—0. 46	141	233. 6	1500

From this table of errors a fully satisfactory inference of the value of the experiments made can be obtained. δM and δS and their relative values are primarily of interest. They indicate the degree of precision with which the logarithmic calculations must be made in order that the arithmetical operations may be consistent with the accuracy of the experimental data. δM, however, has further importance, inasmuch as this factor enters into most of the formulæ for errors. By far the greater number of these may therefore be made more elegant and more practically serviceable by introducing δM in the manner shown on page 229.

Regarding the introductory measurements v the volume of the bulb and t the fiducial temperature it appears that the volumetric method for the estimation of v described on page 214 is acceptable; for by cautious work with all parts at the same temperature a mean correctness of about 0.1^{cc} in a series of measurements is quite attainable. On the other hand the determination of t, by inserting a good mercury thermometer into the re-entrant tube of the porcelain bulb while this apparatus is in place in the revolving muffle, is less satisfactory than it is convenient; but in a series of three or four such measurements a mean error greater than 0.5° C. is improbable. It is understood that it has not been my object in this paper to push measurements of v and t to the extreme fineness desirable; but it is quite clear that this may be done by water calibration and immersion in water.

Greater difficulty is encountered as we approach the main data of measurement, V_1, T_1, H. Since V_1 must be measured throughout with an accuracy of about 0.5^{cc}, it is obvious at once that stages of practically constant temperature, or of very slow heating and cooling, are necessary for measurement. This is attainable in the revolving muffle very perfectly by proper manipulation of the graduated faucet for gas influx and by closing all apertures of the furnace during cooling. With due care, however, the measurement of variable V_1 to 0.05^{cc} will remain a problem of nice observation, particularly so since the total range of variation of V_1 is nearly 235^{cc}. The difficulty is increased, inasmuch as T_1 must be known to 0.1° C.; hence it is not only desirable to jacket the tube *B C* (Fig. 40) with a current of circulating water, but small thermometers adjusted *within* the calibrated tube in such a way as to indicate the temperature of the air inclosed are a desideratum. Fortunately the hot air which emerges from the air thermometer may be completely cooled after passing through the metallic capillary tubes. It appears, moreover, that 150^{cm} of platinum capillary tube of the dimensions given in Table 42 are not seriously detrimental in producing slight differences of pressure in the bulb and manometer; for if V_1 be constructed as a function of T (thermo-electric) by aid of the data in Tables 58 to 66 it will be seen that V_1 obtained during the stage of increasing temperatures (*i. e.*, with the gas on) is quite the same as the corresponding V_1 obtained during the stage of decreasing temperatures (i. e., during cooling), cæteris paribus. This is a crucial test, which reflects favorably on the method as a whole. Fortunately the value of H, or the barometer, is sufficiently given if measured to 0.01^{cm}. This is not only easily done, but an interval of pressure of 0.01^{cm} is larger than the friction of the gas passing through the capillary tubes can maintain for any interval of time as long as that of an observation.

The magnitudes of the corrective term S have already been referred to. It is seen that an error as large as 30 per cent. in v' is without serious effect on the result. In like manner S itself is sufficiently known to 50 per cent. It is this fortunate result which makes the use of a compensator a questionable desideratum; and if it be borne in mind that the distribution of internal fissures is usually such that two stems identical externally are by no means so internally, it is probable that here no advantage is derived from the compensator. This remark refers, of course, to apparatus of porcelain. In the fire-clay air thermometer the porosity of stem will doubtless be greater and the compensator corrective essential.

Finally, it is seen that β measured correctly within 5 per cent. is satisfactory. Concerning both α and β much that has been said above is here applicable (Cf. page 198.)

Accuracy of the measurements made.—After this tolerably full analysis of possible errors, the degree of certainty with which the present data attest the excellence of this method of air thermometry and of pyrometric comparison employed may be satisfactorily discerned. It is expedient to use the graphic tabulation Figs. 41 and 42, in which all the data in question have been inserted.

Let us consider the result for Bulb No. 1 first. The points belonging to the divers Series I to IV for Bulb I are marked with numerals; moreover, when temperature increases (gas on) the numeral is placed above the point; when temperature decreases (gas off, furnace cooling) the numeral is placed below the point. In this way the amount of information contained in the diagram is much increased. With respect to Series I the remark has already been made that but a single thermometer was used in measuring T_1. Now, the temperature of a room in which furnace experiments are being made certainly differs in temperature by as much as 1° for a vertical height as great as $B\ C$, Fig. 40 (150^{cm}). Hence the exceptionally lateral position of the series of points marked "1" is easily accounted for. Nor was a correction applied in these cases for permanent variation of the volume v_0. Again, in Series II an accident by which the thermo-couple was withdrawn from the air-thermometer bulb cooled the electrical apparatus abnormally. This occurred during the stage of decreasing temperature, and the lateral position of certain points marked "2" on the diagram is also accounted for. The remaining points are grouped in close proximity to a uniform locus. The maximum elongation of any of the points, 2, 3, 4, in question is not greater than 10°, whereas, as a rule, this difference is very much smaller. At the outset it is to be borne in mind that into this aggregate maximum discrepancy of 10° are crowded all the errors of the thermo-electric measurement, to say nothing of the errors incurred by the double graphic interpolation by which Fig. 41 was derived from the individual time series of observations of e and T. Of course, results of this kind are susceptible to great improvement if the observations are made by a number of observers instead of by one observer only, for in this way the time error may be eliminated, and observations may be made simultaneously. Quite apart from these considerations an error of 10° is easily incident to the method in its present stage of experimental development. However carefully the manometer may be screened from the furnace an error in T_1 of 0.2° C., or even more, is not improbable; nor was the attempt made to measure V_1 with greater precision than 0.1^{cc}. This already accounts for half of the observed maximum error, apportioning the remaining four or five degrees to the variety of discrepancies already enumerated, to which may be further added changes both of v, the capacity of the bulb, and of β, due to vitrification or similar progressive change of the substance of the porcelain during successive heatings; to irregular differences of the stem error; to the possible occurrence of minute capillary leakage throughout the considerable length of connecting tube; to structural changes (crystallization, silicification, gaseous corrosion) of the metal of the thermo-couple. It is needless to make further mention.

Considering the figures 41 and 42 as a whole, it will be seen that the calibration curves are regular throughout In case of the 20 per cent. platinum-iridium alloy, therefore, no evidence of sudden allotropic changes or polymerization is anywhere discernable. Hence between 300° and 1,300°, the availability of the given platinum-iridium alloy for thermo-electric pyrometry can not be disputed. I do not believe that the strictures which Le Chatelier (l. c.) has placed on the pyrometric use of the platinum-iridium alloys are substantiated by experiment, though they may be true (Chap. I) for low percentage alloys. A full discussion of the divergence of the said curves (Figs. 41, 42) from the Avenarius-Tait equation, is beyond my present purpose.

Accuracy of the measurements made, Group II.—In a general way these critical remarks apply to the data obtained with Bulb II and inserted in the chart (Fig. 42). The method of designation is clear, the divers series being distinguished on the chart by dashes, which pass upward or to the right for ascending temperatures, and pass downward or to the left for descending temperatures. As a whole, the data for Bulb II are a marked improvement upon the data for Bulb I. This was brought about principally by correcting the calibrated volume of the bulb by such permanent changes of volume as occur after each heating. Fortunately the value of this correction can be found with great accuracy and facility by the same method by which the fiducial temperature is determined (cf. page 213). If δv be the permanent alteration of the volume of the bulb due to heating; if b_b and t_b be the pressure and temperature before heating, and b_a and t_a the pressure and temperature after heating, for which, in each case, the air is wholly in the bulb and capillary stems (*i. e.*, $V_1=0$); and if $\Sigma(v)$ be the total original volume of bulb and capillary stems, then

$$\frac{b_b f(t_b)-b_a f(t_a)}{b_a f(t_a)}=\frac{\delta v}{\Sigma v}.$$

The quantity $bf(t)$ occurring in this equation is the same already evaluated in equation 6 (page 213). The following tabular exhibit of the values of δv in question was obtained from Bulb II.

TABLE 77.—*Permanent volume variations of bulb.*

	$bf(t)$	$\frac{\delta v}{\Sigma v}\times 10^3$	v_0	Mean volumes v_0
			cc.	*cc.*
Before Series I	72.677	+6.98	281.26	......280.18
After Series I	73.240	−0.71	279.10	......279.20
After Series II......	73.188	±0.00	279.30	......279.26
After Series III.....	73.210	−0.30	279.22	..... 279.27
After Series IV	73.180	+0.11	279.33	......279.32
After Series V	73.188	±0.00	279.30	

The values of v_0 in the last column are therefore the closest approach to the respective zero volumes of the bulb during the successive series I to V in question. It is this corrective which makes the results[1] of Fig. 42 very much more uniform than those of Fig. 41.

If Fig. 41 be compared with Fig. 42 it will be seen that the agreement of loci is very good. It is clear, beyond question, that the discrepancies involved are those incidental to the measurement; discrepancies, moreover, which are capable of considerable reduction by improving the experimental appurtenances in the way suggested above. It therefore follows that the degree of identity of the environment of the air thermometer and of the thermo-couple is as nearly perfect as the calibration problem demands. Again, from the difficulty I have found in obtaining accordance between different series of results in the earlier experiments, I believe that with the use of the present form of re-entrant bulb the calibration problem has for the first time been rigorously solved; for it is obvious that if the constants of either of the loci (Figs. 41 or 42) were calculated by the method of least squares their probable error would be decidedly within one pro mille.

Boiling point of zinc.—This is the stage of progress at which my other duties will make it necessary to temporarily abandon the temperature problems and proceed toward a corresponding development of the pressure work. I need merely notice therefore in what respects the absolute data of this chapter substantiate the earlier inferences. For instance, if the values of e_{20}, which hold for the boiling point of zinc given at the end of Chapter II, be interpreted by aid of the final dia-

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[1] A curious source of error may be noted here. When the centrifugal blower is insulated the friction of the belt electrifies it permanently. If, furthermore, the tubing be insulated the furnace will be charged with a current of electrified air. Through the wires of the thermo-couple this charge is distributed over the measuring apparatus. If now, any metallic part of this (for instance, the metal of a rheostat key) be touched with the finger there results a redistribution of the charge and invariably a large *deflection of the galvanometer needle*. This is seriously misleading, and the error is not always at once detected. Care should therefore always be taken that the tube conveying air to the furnace from the blower is *not* insulated.

grams (Figs. 41 and 42) the data so obtained are small, being not larger than 905° in the one case and 916° in the other. These values are to be finally corrected by the value for v_0, found after the completion of the measurements by direct water calibration. I may remark in passing, that the stem correction is negative, and that I applied a value which is certainly not too large. Hence the stem error has produced no erroneous negative increment of the value of T.

In the case of Bulb I, the datum v_0 is accepted as 280^{cc}, an approximate value to be subsequently corrected for permanent changes of volume, etc. By the volumetric method (page 214) the volume of bulb, stem, and capillary tubes is found to be 280.73^{cc} at the mean temperature 20°. From this is to be deducted the volume of the metallic capillary stems, 0.40^{cc}; the volume of the porcelain capillary stem, 0.53^{cc}; and the amount of dead space at the joints of the tubes, 0.23^{cc}. This leaves for the volume of the bulb at 0°C.

$$v_0=279.58^{cc}.$$

The same volume was measured at the close of the work by direct calibration with water, and found to be

$$v_0=279.06^{cc}.$$

This difference of 0.52^{cc} is due to the imperfection of the volumetric method in its present form. Preferring the latter value, the volume increment for Bulb I is

$$\delta v=-0.94 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(I)}$$

In the case of Bulb II, v_0 is accepted in the computations provisorily as $v_0=279.3^{cc}$, and found by direct calibration with water to be

$$v_0=278.73^{cc}.$$

Hence for Bulb II

$$\delta v_0=-0.57 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(II)}$$

If now the formula, page 229, viz:

$$\delta T=-\frac{f(T_1)}{\alpha\, v^2}V_1(1+\alpha T)^2\,\delta v$$

be applied with the purpose of correcting the above approximate value for the boiling point of zinc, it appears since $T=910°$; $T_1=25°$ $f(T_1)=0.916$; $v=279^{cc}$; $v_1=220^{cc}$; $(1+\alpha T)^2=19.2$; that

$$\delta T=+12.5° \text{ for Bulb I, and } \delta T=+\ 7.6° \text{ for Bulb II.}$$

In place of the single data obtained from Figs. 41 and 42 it is preferable to determine the values of T for each series. This is done in Table 78, in which, moreover, the data for increasing and decreasing temperature are distinguished. The table applies for $e_{20}=11{,}000$ microvolts, the value found in Chapter II as the equivalent of T.

TABLE 78.—*Interpolations near the boiling point of zinc.*

Bulb.	Series.	T temperature increasing.	T temperature decreasing.	Mean T.
		°	°	°
I	III	912	915	909.0
I	IV	900	....	
II	I	925	....	918.8
II	II	....	916	
II	III	....	924	
II	IV	....	915	
II	V	914	....	

Hence, if to these mean values be added the corrections δT as just found, there follows $T=921.5°$ for Bulb I and $T=926.4°$ for Bulb II.

A final correction is still to be added. In the present reduction I assume $e_{20}=11{,}000$ as the electrical equivalent of the boiling point of zinc. The careful crucible experiments made soon after the air thermometry, and detailed on page 123, show that $e_{20}=11{,}074$. Hence, since

$$\delta T = \delta e_{20}/(a + 2bT)$$

nearly, and since $\delta e_{20}=+74$, it follows that

$$\delta T = 4.7°.$$

The constants a and b are calculated from the data of diagram (Fig. 42), a sufficient approximation. Hence, finally,

$T=926°$ for Bulb I, and $T=931°$ for Bulb II.

This is the closest approximation to the boiling point of zinc which the method, in its present stage of development, permits.

This is a low result as compared with Deville and Troost's, and with Weinhold's data. It agrees admirably with the values of Becquerel and of Violle. But my datum is not as low as would have been anticipated from the constant-volume measurements (page 199) of this chapter, or from inferences deduced by purely thermo-electric measurement in Chapter II. As long, however, as rigorous measurement of the variable β, the coefficient of expansion of the bulb, has not been made, and the effect of a non-glazed interior of the bulb has not been placed beyond all obscurity, it is wise to advert to the present value for the boiling point of zinc with only precautionary emphasis. Nevertheless, it is pleasant to note this accordance of data between the results of the French observers mentioned and my own data. I am specially encouraged in believing the non-inglazed thermometer bulb nearly as available and safe for high temperature measurement as the inglazed form.

Coefficient of heat expansion of porcelain.—It is necessary to state that in the present work no special measurements for β have as yet been made. The value taken is that of Deville and Troost, which, for the porcelain in hand, is possibly too low. The probable effect of correcting β will therefore be an increase of T, since increments of both β and T have like signs. Not wishing at present to redetermine β I made corroborative tests in the following manner:

In Table 66 results are given from which approximate values of the coefficient of expansion of porcelain may be computed. Let the manometer volume be changed when the temperature of the bulb is nearly constant. Then if

$$H_1,\ V_1,\ T_1, \text{ and } H_2,\ V_2,\ T_2$$

are two successive readings, it follows that

$$\left[f(T)+\Sigma\left(\frac{v'}{v}f(T')\right)\right]=\frac{\frac{H_2V_2}{v}f(T_2)-\frac{H_1V_1}{v}f(T_1)}{H_1-H_2}$$

where T is the temperature and v the zero volume of the bulb. It is expedient to make H_2 the barometric height for the day, so the T can at once be computed by the ordinary formula. β may then be computed for $f(T)$. By making the measurements for T (*i. e.*, H_1, V_1, T_1) alternate with the measurements for β (*i. e.*, H_2, V_2, T_2) in time series, the value of T, which corresponds to the time at which the measurements for β are made, may be accurately determined by graphic interpolation. The following results are computed from the data already given in Table 66, Bulb II, Series V:

TABLE 79.—*Coefficient of heat expansion of porcelain.*

Time.		T	β
h.	*m.*	°	
11	45	568	
11	53	(564)	0. 000022
12	03	560	
12	06	(564)	0. 000026
12	25	567	
2	34	978	
2	50	(993)	0. 000037
2	58	1002	
3	10	1004	0. 000027
3	16	1006	

In view of the fact that the quantities on which β ultimately depends are of the same order of magnitude as the stem error Σ, this method of determining β can not be looked to for very close results. Indeed, if

β were known from special measurements this value could be used to compute Σ. It is obvious therefore that for sharp values of β it is necessary to work with a jacketed manometer, so that T_1 may be constant. It is necessary also that T and H be constant, a condition which the above experiments do not quite fulfill. The above data, crude as they are, show, however, that β is determinable by this method with the same degree of accuracy with which it is to be applied. *In this respect the constant-pressure method is unique, since it admits of easy modifications by which the zero volume of the bulb, its coefficient of expansion, as well as all permanent changes of volume, may be evaluated without extra appliances.* [Attention may again be directed to the independent method of standardization of a non-inglazed re-entrant porcelain air-thermometer bulb by thermal comparison with a re-entrant glass thermometer bulb of known constants. Such comparison is to be made above 300° to obviate the moisture and condensation errors, and either directly in the elliptic revolving muffle (Fig. 36 *a*), or indirectly through the intervention of the same thermo-couple. In the last case each bulb is separately compared with the couple as explained above (Figs. 37, 38), and the results then co-ordinated. The hard-glass bulb, according to Troost (loc. cit.) may be safely regarded rigid as far as 600°. 1889.]

Remarks.—The manner of further development of the present thermal problems is now sufficiently obvious, and may be briefly summarized in a final remark. It is necessary in the first place to rigorously compare bulbs glazed interiorly with bulbs not glazed interiorly. The latter are so much more easily constructed that if their use be warranted practical air thermometry will be in no small measure facilitated. For instance, if we suppose the bulb non-glazed interiorly to be admissible, then there are no serious obstacles in the way of a fire-clay thermometer bulb. Bulbs of such ware are naturally porous, but there is no doubt that enamel can be applied in sufficient quantity to the exterior to make them impervious to air. With these bulbs the upper limit of possible thermal measurement will closely approach the melting point of platinum. By aid of the volumetric method described on pages 195 and 214, problems referring to the internal volume of the bulbs and stems, whether porous or not, admit of satisfactory solution. Again, it is necessary to compare the data of bulbs containing different gases, dry air, O_2, H_2, N_2, etc. All such comparisons can be made either directly, by exposing the bulbs contiguously in an elliptic revolving muffle of the kind sketched and described on pp. 182, 188, or they may be made indirectly, by comparing the individual air-thermometer bulbs with the same thermo-couple. In the interest of greater accuracy the same re-entrant form of bulb, into which the divers gases are successively introduced, is expediently combined with one and the same thermo-couple, and the heating is conducted precisely in the manner shown in this chapter. Until Charles's law has in this way been tested for large ranges of temperature it is hardly desirable to multiply the number of approximate thermal data in the region of high temperatures by further data of an absolute kind, which at the present state of our knowledge must also be regarded as approximate. The first steps of a method by which rigorously accurate data may be reached the present chapter fully elucidates.

For purposes of ordinary high-temperature measurement the constant-pressure method of air thermometry must undoubtedly be preferred. It is superfluous to reiterate the many reasons which the text contains. But for the ulterior and purely scientific purposes of studying laws relative to the expansion of gases at high temperatures, both methods are equally valuable, and it is highly probable that an investigation of the thermal-expansion phenomena of one and the same gas in all admissible states of tenuity will throw more light on the subject in hand than an inquiry into the analogous behavior of different gases. Fortunately, in all such comparisons the stem errors so nearly counterbalance each other as to make it probable that the measurements can be made with great nicety.

CHAPTER V.

THE PYROMETRIC USE OF THE PRINCIPLE OF VISCOSITY.

INTRODUCTION.

Remarks.—It has been said that a method for making metallic capillary tubes was described hypothetically by Regnault in his celebrated memoir.[1] So far as I know, however, the first platinum tubes made for actual high-temperature use are those described in the present volume. The dimensions of the capillaries used in the air-thermometer work have already been given; similar tubes of silver and of copper were also in hand. It seemed expedient therefore in view of the excellent quality which these tubes eventually came to possess, to put them to more general use than originally contemplated. Indeed, the attempt to obtain absolute thermal measurements in the region of high temperatures, from the transpiration data obtainable by passing gases through red-hot capillary tubes of platinum, presented itself as an important final step in the present investigation. The kinetic theory of gases has not, as yet, given any satisfactory clue for the prediction of the thermal relations of gaseous viscosity. It is nevertheless probable, from the nature of a gas, that an experimental law, which might be found to hold between 0° and 1,200°, could be safely assumed to hold for a much larger interval of temperature. In other words, judicious extrapolation is much more nearly permissible in the case of thermal results applying to gases than it possibly can be in the case of results which apply to liquids or to solids. Again, since the rate at which transpiration takes place varies inversely as the absolute temperature of the gas, as well as inversely as its viscosity, it is clear that the construction of a transpiration pyrometer will be practicable, even if the thermal variations of viscosity should prove unfavorable for such a purpose.

Apart from practical applications, however, physical science can not but profit by any attempt at high-temperature measurement, rationally based on some other phenomenon than the thermal expansion of a gas. This is proven, for instance, by the pains which V. Meyer, Troost, Berthelot, and others have taken to ascertain whether the coefficient of thermal expansion in all its high-temperature applications could be assumed to be rigorously constant. Even if the present method should fail of further purpose than the co-ordination of data in a field of high temperature, where absolute results are either isolated or wanting, its

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[1] Cf. pages 167, 169.

conditions of application deserve most careful scrutiny. I am justified in believing that the favorable character of the results which this chapter contains will be sufficient to show that the transpiration pyrometer is more than equal to the demands made upon it. Interpreted by the Poiseuille-Meyer formula transpiration data must enable us to measure temperature absolutely, over a wider thermal range, and with greater convenience and accuracy than is now possible with any other instrument.

An important part of the present chapter is the new light it throws on the thermal relations of viscosity and on the thermal relations of the mean free path of the molecule of a perfect gas. The phenomena of diffusion, heat conductivity, and viscosity in gases, depending, as they do, in their thermal relations on the law of force between the molecules, have hitherto remained beyond the reach even of theory.

The present chapter is divided into two parts, the first of which contains experiments made with true capillaries. The second part contains experiments with tubes of larger bore—with tubes, in other words, which do not strictly satisfy the capillary conditions of the Poiseuille-Meyer law.

Literature.—The work of the earlier observers has recently been discussed with great thoroughness by Mr. S. W. Holman[1] in the last of his fine treatises on the relation of viscosity of gases and temperature. Profiting by this, I will therefore dismiss the subject with a few cursory remarks, and refer those desiring more specific information to Mr. Holman's researches. Historical reference is also made in O. E. Meyer's[2] extended article, where the salient features of Graham's[3] classic experiments are analyzed. A clear account of the whole question is given by Meyer in his well-known book.[4]

Some years after Graham had published his experimental results, and after Clausius[5] had pointed out the kinetic importance of the mean free path traversed by the gaseous molecule, the questions relating to the viscosity of gases were placed on a new theoretical footing by the remarkable results of Maxwell.[6] Using Stokes's[7] results to treat the viscosity of air, Maxwell is able to express the mean free path of the molecule absolutely. The data here in question were derived by Cou-

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[1] S. W. Holman: Proc. Am. Acad. Arts and Sci., vol. 21, 1886, p. 1; Phil. Mag., London (5), vol. 21, 1886, p. 199.

[2] O. E. Meyer: Pogg. Ann., vol. 127, 1866, pp. 253, 353.

[3] Graham: Philos. Trans. Roy. Soc., London, 1846, p. 573; ibid, 1849, p. 349; Ann. der Chem. und Pharm., vol. 76, 1850, p. 138.

[4] Die kinetische Theorie der Gase, Breslau, 1877, p. 123.

[5] Clausius: Pogg. Ann., 4th series, vol. 15, 1858, p. 239.

[6] Maxwell: Rept. 295th Meeting Brit. Assoc., 1859 (1860), notices, etc., p. 9; Phil. Mag. (4), vol. 19, 1850, p. 19. Less closely allied results in Phil. Mag. (4), vol. 20, 1860, p. 21.

[7] Stokes: Trans. Cambridge Philos. Soc., vol. 9, 1850, p. 166; ibid., vol. 10, 1851, p. 105. Fortschr der Physik, 1850: 50; p. 101; Phil. mag. (4) I, 1851, p. 337.

lomb's method of vibrating plates, a method which does not serve well for the determination of the thermal relations of mean free path, although it has been applied with this end more or less fully in view by Meyer,[1] by Maxwell[2] himself, by Puluj,[3] and others. Among these observers only Puluj, using an apparatus devised by Kundt and Warburg, succeeded in deriving good results. Very important service was therefore done to this branch of molecular kinetics by the elaborate researches of O. E. Meyer.[4] Availing himself of the general differential equations for the motion of a viscous fluid published by Stokes,[5] or those more recently published by Stefan,[6] O. E. Meyer deduces the well-known equation, in which the rate of transpiration is fully expressed in terms of the terminal pressures, the viscosity of the gas, the coefficient of external friction, and of the dimensions of the capillary tube through which the gaseous flow takes place. Calculating from this result the volume of gas transpiring during a given time, under given conditions, Meyer reaches a result which, for gases, is the complete analogue of the law for liquids experimentally deduced by Poiseuille[7] and Hagen,[8] and to which Stokes[9] and others (Neumann, Wiedemann, Hagenbach, Stefan, Helmholtz) have given a theoretical foundation. It is by using this equation that Meyer[10] himself, discussing Graham's results, in later work,[11] partly in conjunction with Springmühl,[12] derived the first good results for the thermal coefficient of viscosity. Such results have since been obtained in greater number and with greater elegance in transpiration experiments, made by Puluj,[13] v. Obermayer,[14] E. Wiedemann,[15] Warburg,[16] Schumann,[17] and particularly by Holman,[18] to whose elegant and elaborate researches I have already referred.

In all of these cases, however, the data in hand are essentially low-temperature results. The largest range of temperatures occurs in Obermayer's later research, in which the thermal relations of the vis-

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[1] O. E. Meyer: Pogg. Ann., vol. 125, 1865, p. 177; 5th series, vol. 23, 1871, p. 14.

[2] Maxwell: Phil. Trans., 1866 (I), p. 249.

[3] Puluj: Wien. Sitzungsber., vol. 73 (2), 1876, p. 589.

[4] O. E. Meyer: Pogg. Ann., vol. 127, 1866, pp. 253, 353.

[5] Stokes: Trans. Cambridge Philos. Soc., vol. 8, 1847, p. 287.

[6] Stefan: Wien. Ber., vol. 46 (2), 1862, p. 8.

[7] Poiseuille: Mèm. Sav. Étrang., vol. 9, 1846, p. 433; Ann. ch. et phys. (3), vol. 7, 1843, p. 50.

[8] Hagen: Abh. d. Berl. Akad., 1854, p. 17.

[9] Stokes: Trans. Cambridge Philos. Soc., vol. 8, 1847, p. 287.

[10] Meyer: Pogg. Ann., vol. 127, 1866, p. 367.

[11] Meyer: Pogg. Ann., vol. 148, 1873, p. 1; ibid., p. 203.

[12] Meyer u. Springmühl: ibid., p. 503.

[13] Puluj: Wiener Sitzungsber., vol. 69, p. 287; vol. 70, p. 243, 1874.

[14] V. Obermayer: Wiener Sitzungsber., vol. 71, 1875, p. 281; vol. 73, 1876, p. 433.

[15] E. Wiedemann: Fortschr. d. Physik, vol. 32, 1876, p. 206.

[16] Warburg: Pogg. Ann., vol. 159, 1876, p. 403.

[17] O. Schumann: Wied. Ann., vol. 23, 1884, p. 353.

[18] Holman: Proc. Am. Acad. Arts and Sci., vol. 12, 1876, p. 41; ibid., vol. 21, 1886, p. 1.

cosity of a number of gases are studied between —21° and 280°. Mr. Holman's later researches go as far as 224° for CO_2 and 124° for air. E. Wiedemann observed in thermal baths of steam (100°) and aniline vapor (185°). Hence, if the transpiration data are eventually to subserve the purposes of temperature measurement, it is necessary in the first place to investigate the law of variation of viscosity and temperature for a range of variation extending above 300° as far as possible into the region of white heat.

Since this law is necessarily a fundamental consideration it will be inexpedient to report my work in the chronological order of development. It will be preferable, first, to give such results as have an immediate bearing on the law in question, and then to extend the work by an investigation of the flow of gases through tubes to which the term "capillary," taken in the sense of the conditions under which Meyer's formula holds, does not strictly apply. For very short tubes Navier[1] investigated the theory of efflux; for very long tubes these conditions are equally well known from the stated investigations of Poiseuille and Meyer. For tubes of intermediate dimensions, however, the information in hand is comparatively meager, although recent investigations of a relevant character have been published by Osborne Reynolds,[2] by Guthrie,[3] and by Hoffmann.[4]

TRANSPIRATION SUBJECT TO THE POISEUILLE-MEYER LAW.

APPARATUS.

General disposition of parts.—The great degree of perfection which Professor Richards[5] has attained in his jet aspirators suggests the use of this apparatus in the present experiments in a manner similar to that employed by Holman. Such adjustment was at first contemplated. Reasons, however, into which I need not enter here, together with the fact that in some of the experiments larger pressures were demanded than those which the jet-pump could furnish in our laboratory, led to the employment of absolute methods and of the special apparatus now to be described. It consists essentially of two large vessels, one placed as far as may be necessary above the other and connected by wrapped rubber tubing. The upper of these vessels is filled with mercury and the lower contains the dry air to be forced through the train of capillary tubes in connection with it. In this way a column of mercury of any desired height is brought to bear on the lower vessel, and the details of adjustment are then to be such that this pressure may remain constant throughout the course of the experiment.

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[1] Navier: Mém. Acad. Roy. des Sc., vol. 9, 1830, p. 336.

[2] O. Reynolds: Roy. Inst. Gr. Brit., 1884, p. 1; Beiblätter, vol. 10, 1886, p. 217.

[3] Guthrie: Phil. Mag., 5th ser., vol. 5, 1878, p. 433.

[4] Hoffmann: Ann. der Physik, Wiedemann, new series, vol. 21, 1884, p. 470.

[5] Richards: Am. Jour. Sci., 3d series, vol. 8, p. 412; Trans. Am. Inst. Mining Engineers, vol. 6, 1879, p. 492.

In Fig. 43 the apparatus for producing the pressure in question is fully given. The scaffolding consists of four vertical tubes of gas pipe, *ab*, *ab*, *ab*, *ab*, about 15^{cm} apart and 200^{cm} high. They are screwed below to a suitable base and coupled together above, forming together a long rectangular column of square section. The tops of each tube end in vertical and lateral screws *a*, *a*, *a*, *a*, to which similar pipe may be attached, either vertically or horizontally, thus greatly increasing the efficiency of the standard either for the present purposes or for use in supporting the manometer tubes of an air thermometer (cf., pp. 168, 209). The two vessels for mercury are shown at *A* and *B*, of which *B* is stationary, while *A* can be raised to any necessary height by the cord *F G H* passing over the pulley *G* and fastened by a flat-headed thumbscrew, *H*. The vessel *A* is practically a Mariotte flask, provided with a stop-cock at *C*. *B* has a similar stopcock at *D*, and the connecting rubber hose is shown at *C E D*. These connections, in addition to the stop-cocks *C* and *D*, should be of wide bore, so as to insure a nearly frictionless flow of mercury.

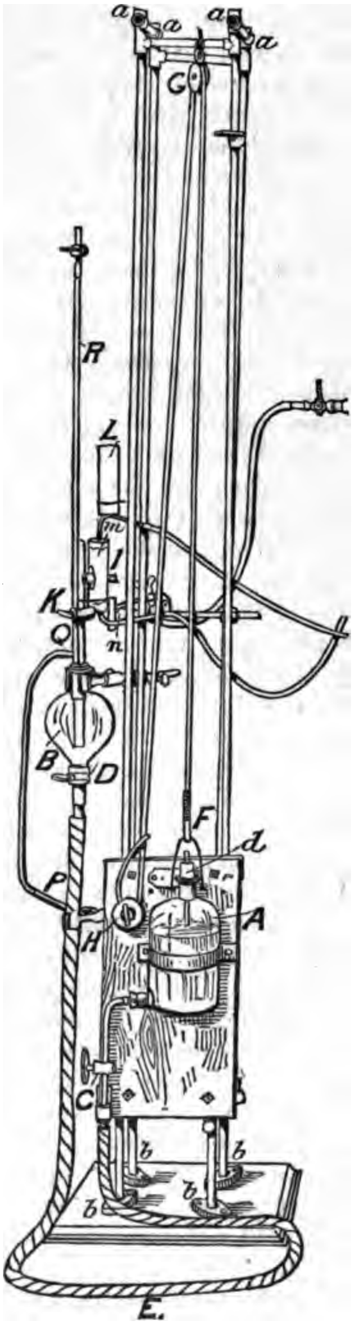

FIG. 43. General disposition of apparatus for viscosity measurement. Scale $\frac{1}{13}$.

The head of the vessel *B* communicates with the capillary tube *I*, carries the open mercury manometer *R* for the measurement of pressures, and is in connection with a stop-cock (not shown in figure), by means of which atmospheric air or any other gas may be introduced into *B* through a desicating tube. As this will be more clearly shown in the diagram below, I need only say that the capillary tubes are shut off by a faucet, *K*. Finally, a wide lateral tube, *P Q*, in communication with the rubber hose at *P*, enables the observer to let the mercury flow into the receiver *B from above* by closing the stop-cock *D*. As this is the special feature of the present apparatus, and is essential for the maintenance of constant pressure, I will describe it further. Suppose the Mariotte flask *A* to be hoisted in and fixed in the high position; suppose the receiver *B* filled with air, and communication with the atmosphere and with the capillary tubes to be shut off, moreover, the stop-cocks *C* and *D* closed. If now *C* be opened, mercury will flow from *A* to *B* through the hose and the lateral tube *P Q*. The head of mercury urging the influx will be the difference in height between *Q* (the point of influx) and the lower end of the tube *d* in the Mariotte flask *A*. The flow will continue until the manometer *R* registers the equivalent pressure. If, now, the stop-cock *K* of the capillaries be opened, the air from *B* will be very slowly discharged into the atmosphere and the mercury from *A* will slowly flow into the receiver *B*, entering it from above in such a way that the *pressure is maintained constant throughout the course of the experiment;* for the head of mercury between *Q* and the Mariotte level remains unchanged until *B* is quite filled, and the pressure value of the head is read off on the manometer *R*. Special care, however, must be taken with the construction of the Mariotte flask; for inasmuch as the flow from such a flask is necessarily intermittent, the period of intermittence must be reduced to the smallest possible amount by compelling the air to enter *A* through *d* in very small bubbles. The lower end of the tube *d* is therefore drawn out into a capillary of, say, 0.05^{cm} diameter, which is ground off obliquely in the usual way. It is still better to let the lower part of *d* end in a series of capillary platinum tubes, all cut off obliquely, with their open mouths nearly in the same horizontal plane. Air thus enters *A* in a spray of fine bubbles, and the intermittence seen at *R*, even in the most unfavorable cases of extremely slow efflux of gas out of *B*, is reduced to 0.01^{cm} and less.

The air in *B* enters the capillary tube through the stop-cock *K*, as has been said. The capillary platinum tube itself is shown at *I*, and is wound in form of a truncated cone, so as to be uniformly heated by the adjustable burner *n* immediately below it, the gases of which are carried off by the adjustable chimney *L*. In other words, the helix of the platinum capillary tube is so wound as to lie quite within the zone of fusion of the Bunsen burner. The outer end of the tube *I* communicates directly with the air. The other end is soldered into a lateral arm of the tube *K* by means of resinous cement. In order to keep the joint cold and the inner end of the capillary at a known temperature a rapid current of cold water from the hydrant flows through the cylindrical sheet-iron box *m*, which surrounds the joint.

Apparatus for constant pressure.—This form of apparatus was used in the earlier experiments, and the results obtained by means of it, some of which will be cited below, proved the feasibility of this method, at least for empirical temperature measurement, beyond a doubt. In later experiments the proximity of the burner *n* to the receiver *B* was found objectionable, and the cramped arrangement of this part of the apparatus interfered in other ways with accurate measurement. Retaining the essential features of Fig. 43 the apparatus was modified as follows:

In Fig. 44, *B B* is the receiver into which the mercury flows on passing out of the Mariotte flask. The lettering of this figure is in conformity with that of Fig. 43, but the disposition chosen is such as to show additional parts. The manometer *R R′ R′* is here very clearly given, quite filled with mercury, as is the case at the outset of the experiment. It will be seen that as the pressure in *B* increases, the mercury in the reservoir *R′ R′* passes into the tube *R*, leaving a vacant space in *R′ R′* above the lower meniscus. But as the experiment proceeds, and the receiver *B* fills with mercury, this metal eventually falls into the communication tube *r*, while the air displaced escapes into *B* through the capillary tube *s*. Hence each time *B* is filled with mercury a fixed volume of air must pass out of it, and the manometer *R R′ R′* introduces no discrepancy. The cock *D* being closed, mercury falls into *B* from *Q*, as the column passes through the lateral tube *P U Q*. The top of *R′R′* is cut off obliquely, so as to guide the descending drops or little stream of mercury at once into *B*. The drying-tube of the apparatus communicates with *w*, and may be shut off by the faucet *S*. In this way dry air or any other gas may be easily introduced. The capillary tube is here placed at some distance from *B* and in connection with the lateral tube *k*. A small sensitive thermometer sealed in the vertical tube *T* indicates the temperature of the gas as it escapes into the capillaries. For the sake of clearness in diagram the tubes *Q*, *R*, *T* are represented as placed in a single vertical plane. In practice the rubber cork is perforated symmetrically and larger tubes may be chosen. The tube *P Q* comes apart at *U*, and hence the tubes and the manometer may be easily withdrawn from *B*. When in use it is necessary to seal in the cork and the divers glass tubes with resinous cement.

It is easily seen that after *B* is full of mercury the Mariotte flask *A* may be lowered, and on opening the stop-cocks *D* and *S* mercury will flow back from *B* to *A*. The receiver *B* is thus filled with dry gas and again ready for experiment. But the order of manipulation is important, and will be indicated in connection with the data given below.

In using the method of compression preferably to a method of exhaustion, by both of which a flow of gas through the tubes can be secured, I was guided by the belief that the methods of measurement in the former case are more easily capable of variation. This the present chapter may show. Again, the tendency of the dissociated hydrocarbon gases of the burner to permeate the walls of the platinum capillary tubes at high temperatures, is of less disturbing effect when the current of gas is condensed than when it is rarified.

The capillary apparatus.—In Fig. 44 there is ample room for air to

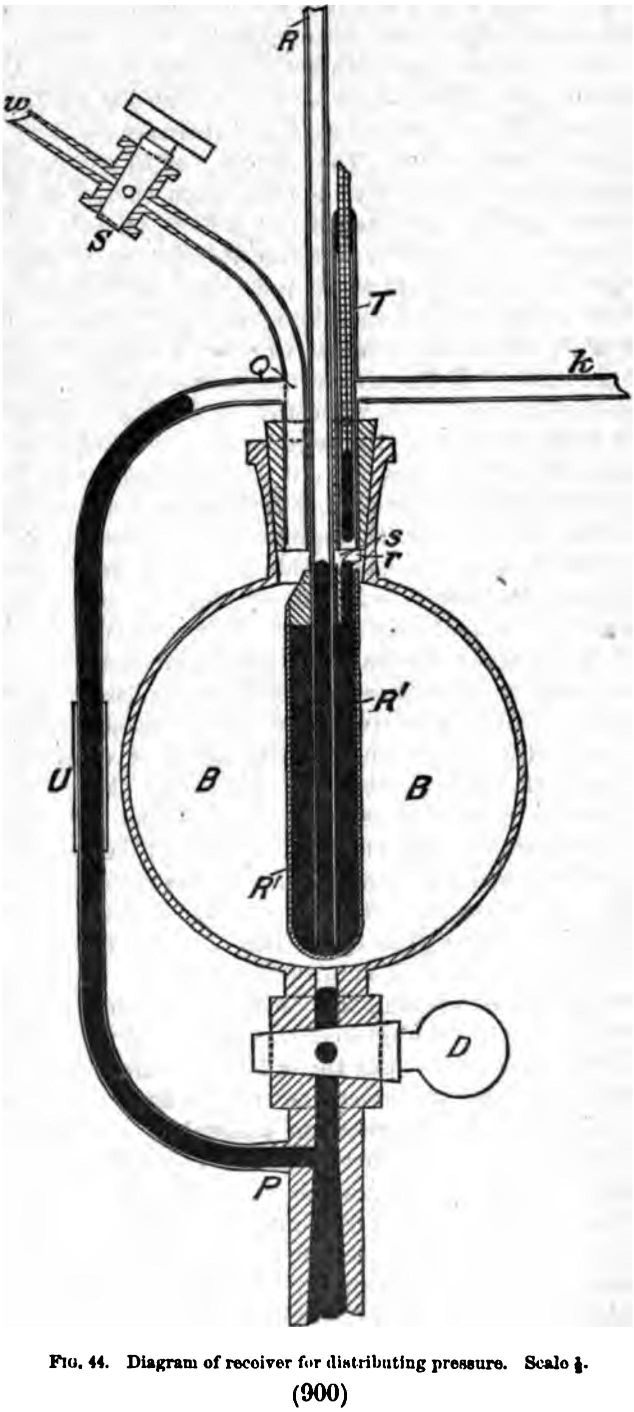

FIG. 44. Diagram of receiver for distributing pressure. Scale ½.

pass around the thermometer in the tube *T*, and thence by the lateral tube *k* into the capillary apparatus. This is shown in side elevation in Fig. 45 and in plan in Fig. 46. The figures are sectional, and the lettering of Fig. 43 is retained. The scaffolding and non-essential parts are omitted. Regarding this figure in its general purposes, I will say here that there are three ways in which viscosity has been measured:

1. By measuring the time of efflux of the fixed volumes of air in *B* through the capillaries.

2. By measuring the rate at which air passes out of the capillaries.

3. By differential methods.

The first of these methods is not generally as convenient as the second, because the volume of *B* is relatively large, and the time of efflux may become enormously large. Hence in my final experiments I used the second method, and it is to this that the present description largely applies. The gas enters from the tube *k* (Fig. 45) through the stop-cock *K*, thence it passes through the tube *g h* into the coil of platinum capillary tube *I*, and out of this into the graduated tube *l l l l*, filled with water. Here it is measured. The tube *l l l l* is simply an inverted burette of about 50^{cc} capacity. After filling it with gas and taking the observation it is made ready at once for the next experiment by sucking the water out of the pneumatic trough *M M* up into the tube through the stop-cock *o* and closing it. To insure constancy of temperature this tube *l l l l* is jacketed by a larger tube, *i i i i*, through which a rapid current of water, entering by the tube *p t*, continually circulates. The water escaping from the bottom of *i i i i* keeps the trough *M M* full of cold water, and finally escapes by the lateral efflux pipe *X*. The upper vertical tube *q* is used in filling *i i i i* with

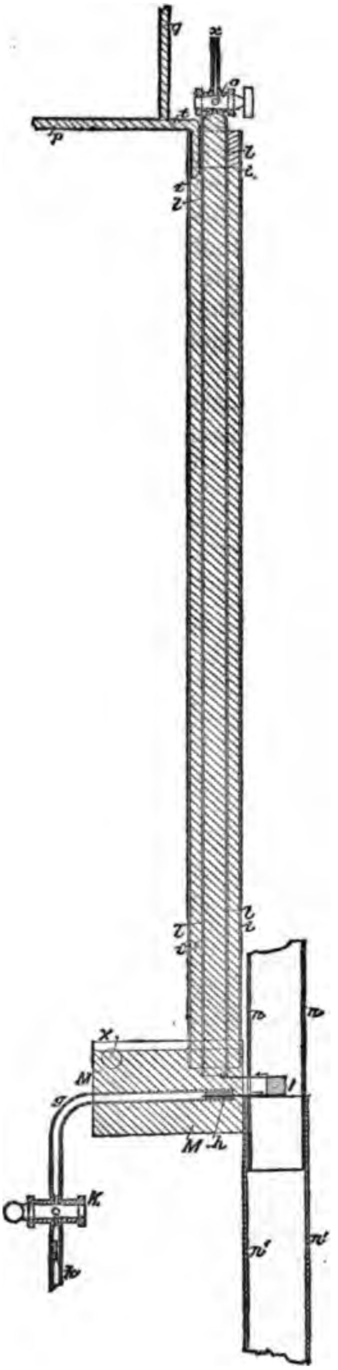

FIG. 45. Side elevation of capillary apparatus. Scale ¼.

water at the outset of the experiment, and is then closed by a pinchcock. It is easy to make the current swift enough to keep both the tube and the trough at a constant temperature even when the helix *I* is heated to extreme white heat.

The helix of the platinum capillary tube is wound in the form of a nearly compact spiral and with the internal radius just large enough to admit the insulator of the thermo-couple. Smaller and more compact coils are favorable to constant temperature throughout the length of the capillary tubes. It is convenient to use two or more such capillary tube, wound side by side, so as to make what may be called a fasciculated helix. The anterior ends of these capillaries are soldered to a small longitudinally perforated brass cylinder *h*, which is then hermetically sealed into the adit tube *g h*. The posterior ends of the capillaries, which, like the other ends, return to the trough *M M*, are bent slightly upward, so as to discharge the gas into *l l l l*. As leaks are fatal to the temperature measurement at *I*, the platinum tubes must be carefully soldered into the vertical wall of the trough *M M*, through which they pass. Soldering the tubes in place and sealing them is a difficult operation, and too much care can not be taken in guarding against clogging of the minute capillary canals. Moreover, solder must be kept away from the parts of *I* which are heated. Insufficiently cautious manipulation in this respect ruined more than one of my tubes. Unfortunately, the only satisfactory check on the degree of perfection of the adjustments made

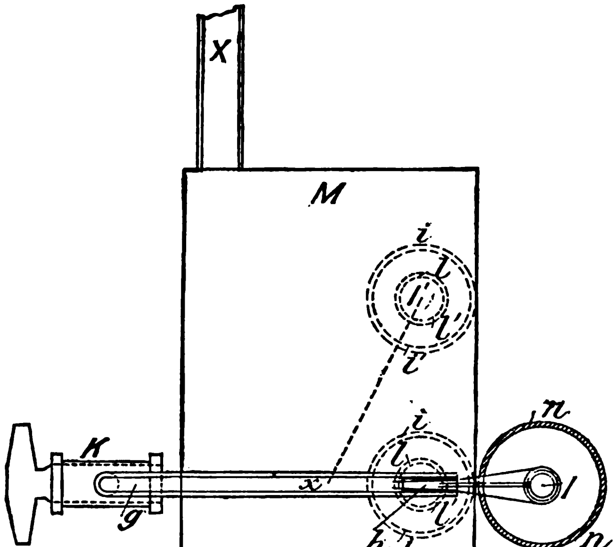

FIG. 46. Plan of the capillary apparatus. Scale ⅓.

is given by an inspection of the results obtained. Any flaw in the connections can therefore be remedied only at the expense of much time.

Differential apparatus.—Before passing to the method used for heating it may be well to insert a few remarks relative to the differential apparatus. This is closely analogous in character to a differential galvanometer, and the rates of transpirations through tubes, one of which is hot the other cold, are compared. The arrangement of this apparatus is readily seen in Fig. 46. A lateral arm, *X I′*, of the tube *g h* communicates with the cold helix *I′*, which is completely submerged in the water of the trough *M M*, and provided with its own graduated tube *l′ l* and water-jacket *i i′*. Except in temperature, the capillaries and their pneumatic appurtenances are identical in form. Certain special desiderata will be indicated below.

Method of heating.—All the soldered parts of the capillary apparatus being thus thermally protected by a current of water from the hydrant, the heating of the spiral is not a difficult problem. To make observations at the low temperature (as near 0° C. as convenient) a current of water may be showered upon the helix out of the water pipes. But it is equally good to siphon the water out of the trough *M M*. For 100° the helix is appropriately surrounded by a non-conducting tube, through which steam circulates freely. Admirably constant mean temperatures are obtained as high as 1,000° by simply heating the helix in a chimneyed Bunsen burner. For 1,300° the Bunsen burner is replaced by a blast-lamp fed by a regular current of air. In the case of these high temperatures the helix is surrounded by a cylindrical tube of asbestus, as shown at *n n*, Figs. 45 and 46. These cylinders are exceedingly convenient and may be made by soaking asbestus board in water and rolling it around a cylindrical stick of suitable diameter. After drying, the cylinders are ready for use. Parts liable to breakage are, of course, protected from radiation by asbestus screens. Such subsidiary screening is everywhere necessary, and need not be described here. Great difficulties were encountered in endeavoring to obtain satisfactorily constant temperatures between 300° and 1,000°. After much vain searching I finally tried an ordinary oil student lamp for the purpose, and obtained excellent results. The space in the chimney of such a lamp above the flame is available for a hot-air bath. In Fig. 45, *n′ n′* shows the position of the chimney of this lamp. The temperatures thus obtainable, besides being constant or of very slow regular variations (increase) may be made to differ over quite a wide range, as is shown by the following table:

TABLE 80.—*Thermal constants of the oil student lamp.*

d	Time.	*e*	θ''	Remarks.
cm.	*m.*		°	
2	0	4168	414	Very low flame.
2	7	4201	416	
2	14	4255	421	
2	21	4288	423	
3	....	7437	669	Low flame.
14	10	7593	681	
14	20	7647	685	
14	30	7784	695	
9	25	10690	904	High flame.
9	30	10690	904	
3	40	9563	825	
3	60	9563	825	
14	63	11490	966	
14	69	11490	956	
Incipient fusion of the glass chimney surrounding the flame. Devitrification.				Flame very high.

In Table 80, *d* denotes the depth of the junction of the thermo-couple *below* the top of the chimney, which top is about 20^{cm} above the mean height of the flame. θ'', *e*, denote the temperature and the corresponding thermo-electric force of the thermo-couple used for measurement at the time given in the second column. The thermo-couple in this instance was No. 39 (calibrated above), and the junction, after being surrounded by a little cushion of carded asbestus, was enveloped by a jacket of thin platinum foil fastened to the stem insulator. The junction is, of course, placed in the axis of the chimney, since temperature decreases towards the walls. The highest temperatures are obtained by enveloping the chimney in the cylindrical tube of asbestus referred to above, in which case the glass is easily fused. Lower temperatures than those of the table may be obtained by lengthening the chimney with the asbestus tube and observing near the top. The auxiliary tubes are suitably wired in position.

In addition to the large interval of temperature, the Argand lamp has the advantage of furnishing an air bath. Since platinum is pervious to hydrogen (see below), direct exposure to the Bunsen flame introduces an error because of the hydrogen which passes through the metal. But this error does not seem to be serious unless the temperatures are very high.

In all these cases the mean temperatures are satisfactorily constant, but it does not follow that temperature will be constant throughout the volume of the platinum capillary. Indeed, variations of 100° within the spires of the helix at temperatures as high as 1,200° are not impossible. If, however, the interior of the helix be filled with some non-conducting substance like asbestus fiber, and the exterior surface be snugly surrounded by a little box of non-conducting substance, like mica, the degree of constant temperature is much improved. Better results are obtainable by surrounding the helix with alternate layers of good and bad conductor. But in its practical application this method is troublesome, and I have therefore preferred to measure temperatures at both the exterior and the interior surfaces of the helix. In the final experiments two thermo-electric junctions were in contact with the outside and one with the inside of the helix.

Pressures were read off in mercury columns by aid of the Grunow cathetometer already referred to. It is frequently necessary in this apparatus to open the stop-cocks at particular pressures. To obtain these, preliminary experiments are made ("*Einschiessen*"), and the desired positions of the meniscus are indicated by adjustable fiducial marks.

For the measurement of intervals of time an excellent chronometer of Bröcking in Hamburg was available.

METHODS OF COMPUTATION.

The general equation.—The computations of the present memoir are based on the Poiseuille-Meyer transpiration formula, the special application of which to gaseous flow is due to Meyer.[1] It is available in two forms. The first form is

$$u=\frac{P^2-p^2}{8\eta Lp}(R^2-r^2+2\zeta R) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where u denotes the velocity of a particle at a radius, r, from the axis of the capillary tube, the diameter (bore) and length of which are $2R$ and L, respectively; where P and p are the pressures at the two ends of the capillary tube, and where η denotes the coefficient of internal friction (viscosity), ζ the coefficient of slip (Gleitung's coefficient). The second form is obtained by integration from equation (1). It contains a new variable, viz, V_1 the volume of gas transpiring through any section of the tube where the pressure is p_1 during the time t.

$$V_1=\frac{\pi t}{16\eta}\,\frac{P^2-p^2}{p_1}\,\frac{R^4}{L}\left(1+4\frac{\zeta}{R}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If this equation is to be used for the absolute evaluation of η it must be borne in mind that the dimensions of $\frac{P^2-p^2}{p_1}$ are those of a pressure. Hence if P and p have been expressed in terms of the heights of columns of mercury, the factor δg must be inserted in the right-hand mem-

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[1] Meyer: Pogg. Ann., vol. 127, 1866, p. 269.

ber. Here δ is the density of the mercury column and g the acceleration of gravity at the place of observation. With this introduction the dimensions of η, computed from equation (2), are $[ml^{-1}T^{-1}]$, which are identical, of course, with the dimensions required by the fundamental formula of viscosity, or by the well-known equation of Maxwell, $\eta=0.318\rho\Omega L$, deduced in the kinetic theory of gases. Equation (2) shows, moreover, that the dimensions of ζ are linear, agreeing with the thermo dynamic interpretation of ζ, which is proportional to the mean free path of the molecule of a gas. ζ has been called "Gleitung's coefficient" by Helmholtz, a name, the appropriateness of which appears, inasmuch as $\zeta=\frac{\eta}{\varepsilon}$ where ε is the coefficient of external friction of the gas.

Neither formula (1) nor formula (2) contain direct reference to the temperature at which transpiration takes place. Such reference is, however, implied in the p occurring in the denominators of (1) and (2); for the value of p is given by Boyle-Charles's law as

$$p=k\rho(1+\alpha\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ρ and θ are the density and temperature corresponding to the pressure p, and where k is constant.

Regarding the general applications of (1) and (2) I will say that the derivation of these equations presupposes that p and ρ are independent of r, or that for the points of any given right section of the tube p and ρ are constant. Again it presupposes a nearly steady flow, such that the differential coefficients of u^2 and $\frac{du}{dx}$, i. e.,

$$u\frac{du}{dx}, \qquad \frac{d^2u}{dx^2}, \qquad \frac{d^2u}{dxdr},$$

where x is measured along the axis of the tube are practically zero. Finally equations (1) and (2) are true only for circular sections. In the case of elliptic sections,[1] with semi-axes a and b, the equation (2) becomes (supposing $\zeta=0$)

$$V_1=\pi t\,\frac{P^2-p^2}{p_1}\,\frac{1}{8\eta L}\,\frac{2a^3b^3}{a^2+b^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that the equation, when a and b are not known, can only be used for the interpretation of relative measurements.

Case of two cold ends, absolute apparatus.—Equation (2) is available for experimental measurement in a variety of ways. It presupposes, however, that the temperature of the capillary tube be the same throughout its length. This is, of course, a feasible precaution, for it is only necessary to weld the platinum capillary to platinum terminal tubes

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[1] Meyer: Ibid., p. 364; Matthieu: C. R., vol. 57, 1863, p. 320.

of larger bore. Methods of doing this will be described below. Such apparatus would, however, be expensive, and in an introductory investigation, in which easy variation of the capillary bore is one of the desiderata, the use of fixed forms of apparatus is unadvisable. Hence I have made use of platinum capillary tubes with cold ends in the way described in the preceding paragraph, inasmuch as these can be drawn down from the original to any smaller radius, and then inserted into the pneumatic apparatus with comparative facility. The cold ends, however, introduce an error of a serious kind, for which allowance must be carefully made. Fortunately this can be done with ease and accuracy by successive applications of Meyer's equation.

As before, let R, L, θ, t be the symbols of radius, length, temperature, and time. Let the platinum capillary tube be supposed to be made up of three parts, l', l'', l''', so that $l'+l''+l'''=L$. Let the variables referring to these parts be similarly accentuated. Then the following scheme of variables presents itself:

$$P\ \underbrace{V',R',l',\theta',t',\eta',\text{etc.}}\ \ p'\ \underbrace{V'',R'',l'',\theta'',t'',\eta'',\text{etc.}}\ \ p''\ \underbrace{V''',R''',l''',\theta''',t''',\eta''',\text{etc.}}\ \ p$$

Of the three partial tubes thus given the first and third are ends, and hence l' and l''' are small as compared with l'', and θ' and θ''' small as compared with the high temperature θ''. Applied to the apparatus described, the following simplifications are admissible: $R'=R'''=R$; $\eta'=\eta'''=\eta$; $\theta'=\theta'''=\theta$; moreover $V'\rho'=V''\rho''=V'''\rho'''=V\rho$, and $t'=t''=t'''=t$. The successive application of Meyer's equations thus leads to .

$$Vk\rho(1+\alpha\theta)\frac{16}{\pi t}\left[\frac{\eta}{R\left(1+4\frac{\zeta}{R}\right)}(l'+l''')+\frac{1+\alpha\theta''}{1+\alpha\theta}\frac{\eta''}{R''\left(1+4\frac{\zeta''}{R''}\right)}l''\right]=P^2-p^2 \qquad (4)$$

Now, if β be the mean coefficient of expansion of platinum, so that $R''=R_0''(1+\beta\theta'')$ (R and R_0 being supposed identical), I find finally that

$$\frac{\eta''}{1+4\frac{\zeta''}{R''}}=\left[\frac{\pi}{16}\frac{P^2-p^2}{p}\frac{t}{V}\frac{R_0''^4}{l''}-\frac{\eta}{1+4\frac{\zeta}{R}}\left(\frac{R_0''}{R_0}\right)^4\frac{l'+l'''}{l''}\right]\frac{1+\alpha\theta}{1+\alpha\theta''}(1+\beta\theta'')^4 \qquad (5)$$

If this equation is to express η'' absolutely, and if P and p are measured in heights of columns of mercury, the factor δg must be inserted in the right-hand member, as before (page 252). Regarding the other quantities it is clear that they are measured in terms of c. g. s. units. The temperature of V is θ.

Equation (5) is capable of much simplification. In the above apparatus $R_0''=R_0$; hence care must be taken either in making $\frac{l'+l'''}{l''}$ as small as possible, or l' and l''' must be correctly measured. In the above apparatus very close contiguity of hot and cold parts of the spiral is secured by the use of running water in the way described. Moreover η is small as compared with η', because long ranges of temperature are met with. In view of the factor $\left(\frac{R_0''}{R_0}\right)^4$ it is obvious that the corrective factor may be made to vanish speedily by selecting terminals of larger bore. If $\theta=\theta''$, and therefore $\eta=\eta'$, equation (5) reduces at once to equation (2), supposing of course that $R_0''=R_0$.

Case of two cold ends, differential apparatus.—With this result in hand the question with regard to the equations applying to differential apparatus of the kind sketched above (page 250) is next in order. For the case of the hot helix there applies as before

$$\frac{\eta'}{1+\frac{4\zeta''}{R''}}=\left[\frac{\pi}{16}\frac{P^2-p^2}{p}\frac{t}{V}\frac{R_0''^4}{l''}+\frac{\eta}{1+4\frac{\zeta}{R}}\left(\frac{R_0''}{R_0}\right)^4\frac{l'+l'''}{l''}\right]\frac{1+\alpha\theta}{1+\alpha\theta''}(1+\beta\theta'')^4$$

and for the cold helix, the temperature of which is uniformly θ,

$$\frac{\eta}{1+\frac{4\zeta}{R_c}}=\frac{\pi}{16}\frac{P^2-p^2}{p}\frac{t_c}{V_c}\frac{R_c^4}{L_c};$$

whence, very nearly,

$$\frac{\frac{\eta}{1+4\zeta''/R''}}{\frac{\eta}{1+4\zeta/R_c}}=\left[\frac{t}{t_c}\frac{V_c}{V}\frac{L_c}{l''}\left(\frac{R_0''}{R_c}\right)^4-\left(\frac{R_0''}{R_0}\right)^4\frac{l'+l'''}{l''}\right]\frac{1+\alpha\theta}{1+\alpha\theta''}(1+\beta\theta'')^4 \quad . \quad (6)$$

Now, if the two helices be identical in radius and length, and if the times of transpiration be also identical, then, since $t=t_c$; $L_c=L$; $R_0''=R_0=R_c$;

$$\frac{\frac{\eta'}{1+\frac{4\zeta''}{R''}}}{\frac{\eta}{1+4\zeta/R_c}}=\frac{1+\alpha\theta}{1+\alpha\theta''}\,\frac{\frac{V_c}{V}-\frac{l'+l'''}{L}}{1-\frac{l'+l'''}{L}}(1+\beta\theta'')^4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Again, if as before, $R''_0=R_0=R_c$, and $L=L_c$, but the same volumes are found to transpire in the times t and t_c; then, since $V=V_c$

$$\frac{\frac{\eta'}{1+\frac{4\zeta''}{R''}}}{\frac{\eta}{1+\frac{4\zeta}{R_c}}}=\frac{1+\alpha\theta}{1+\alpha\theta''}\,\frac{\frac{t}{t_c}-\frac{l'+l'''}{L}}{1-\frac{l'+l'''}{L}}(1+\beta\theta'')^4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

Finally, if $\theta=\theta''$ equation (6) furnishes a very simple equation for the ratio of radii of capillary tubes. For if $t=t_c$

$$\left(\frac{R''}{R_c}\right)^4=\frac{V L}{V_c L_c},$$

a relation which is frequently of use.

EXPERIMENTAL RESULTS.

Manipulation.—In describing the present series of experiments it will be advisable to proceed somewhat explicitly; for the methods were frequently varied, and variations of an apparently trifling kind were frequently found of great practical importance. Neither is it expedient to retain wholly the chronologic order of experiment. The following tables, 81 to 89, represent a connected series of experiments, in which the method used is gradually perfected, and in which the data therefore approach the true law of variation more fully as the experiments proceed.

In making these experiments the apparatus, Figs. 44 to 46, was used. The air which had transpired was therefore caught after efflux from the capillary tubes. Inasmuch as the receiver *B* is very large (550^{cc}) and transpiration through the capillary tube takes place at a very slow rate, almost no effect is produced in the pressure of the gas in *B* when the cock *K* (Figs. 43, 46) is opened. This is a great convenience in manipulation and suggests the following scheme of operations: Suppose the Mariotte flask to be in its lowest position on the standard, *aaaa bbbb*, all cocks except *K* open, and the Mariotte uncorked. Mercury will then have run back into *A*, and the reservoir *B* will be filled with dry air. Now, close the cocks *C* and *S* and cork the Mariotte. Hoist the flask *A* to the level above *B* desired, and clamp it. Open *C* slightly at first until the mercury is seen just above *D* and then close *D*. Mercury will then flow into *B* through *P U Q* (the cock *C* being now fully open) until the maximum pressure is registered by the manometer *R R'R'*. Both the lower and upper meniscus of this are read. The gas in *B* is therefore practically under the pressure under which it is to be passed through the capillaries. Inasmuch as the volume of *B* is more than ten times as large as the volume to be measured after efflux, the pressure apparatus is ready for a number of consecutive experiments. After the receiver is quite filled with mercury and the cock *K* is closed, *C* is closed also and the Mariotte flask is lowered and unstopped. *D* is now opened and *C* is opened cautiously, so as to take the pressure out of the manometer. After this is done *S* is opened, whereupon *C* may be fully opened and the mercury thus flows back to *A*, while *B* fills with dry air. The operations are then repeated and the gas in *B* is put under pressure for the next ten experiments. This is the mode of experimentation in the main, although accidents or divers special purposes suggest slight variations of it. It is desirable to draw no air through the manometer $R R' R'$; for not only will such air be moist, but the mercury hurled out of $R' R'$ by bubbling displaces the lower meniscus to a seriously low level some times. During the experiments the lower meniscus remains constant in level. Hence the upper meniscus need be read only for the detection of slight variations, and the fact that the lower meniscus is finally hid by the surrounding mercury is no disadvantage.

Nomenclature.—The results were computed from equation (5), on page 254. The data in the table are similarly designated, and their full signification is as follows:

P is the pressure of the gas at influx, i. e., when it enters the platinum capillary. P therefore is the zero height of the mercury column in the manometer plus the zero height of the barometer. Correction is to be made for capillary depression of the upper meniscus of the manometer. Correction is also to be made for optic displacement of the lower meniscus of the manometer when seen through the walls of the reservoir B (Fig. 44). As the mean effects produced by these two errors were in an opposite sense, and nearly the same in magnitude, I did not apply them. Moreover they have no effect on $F(\theta'')$.

p is the pressure of the gas at efflux. Hence it is equal to the zero height of the barometer increased by the mercury value of the depth of the efflux tubes below the level of water in the trough. Perhaps p ought also to have been increased by the capillary reaction effect of water at the point of efflux. But as I could not estimate this, I used large values of P in order to secure as steady and rapid a flow as permissible.

t is the time which corresponds to the volume of gas V_0 measured after transpiration. It is usually advisable to make t nearly constant and measure the variation of V_0. The time errors made in opening and closing the stop-cock K are not larger than one-fifth of a second. Hence t can be measured sharply.

V_0 is the volume of dry air escaping at the normal pressure 76^{cm} and temperature 0° C. V (page 248) being the true variable, some pains must be taken in correcting it. In the first place, inasmuch as V is measured over water, it must be reduced to dryness, to zero centigrade, and to 76^{cm}. This is conveniently done by the aid of Landolt and Boernstein's tables, it being remembered that V is under atmospheric pressure minus the mercury value of the residuary column of water in the burette $llll$. Finally V must be corrected for the solubility of the gas, which in case of air may be neglected, but in case of hydrogen is as large as 2 per cent. Formula (5), however, calls for V at θ and p. Hence, if V is reduced at once to 0° and 76^{cm} by tables, it is convenient to transform formula (5) into

$$\frac{\eta''}{1+4\frac{\zeta''}{R''}}=\left[\frac{\pi}{16}\,\frac{P^2-p^2}{76}\,\frac{t''\,R_0''^4}{V_0\cdot l''}-\frac{\eta}{1+4\frac{\zeta}{R}}\left(\frac{R_0''}{R_0}\right)^4\frac{l'+l'''}{l''}\right]\frac{(1+\beta\theta'')^4}{1+\alpha\theta''}$$

which easily results since $\frac{Vp}{1+\alpha\theta}=76.V_0$, and the effect of $(1+\alpha\theta)$ on the corrective member of formula 5 may be neglected, when θ is small.

Finally, V must be corrected for the amount of air left in the adit tube $g\,h$, after the cock is closed. To reduce this dead space to the smallest value it is desirable to fill up the tube $g\,h$ partially with glass rod. The residual space is easily measured, as follows: Let ν be this residual volume. Then, if in the time t, which elapses between opening and closing the cock k, the volume V escapes into the measuring tube, the volume ultimately found there is $a=V+\nu$. Again, if during the same time t the cock had been opened and closed n times (delays of opening and closing supposed to be allowed for) the volume found in the measuring tube is $b=V+n\nu$. Hence

$$b-a=(n-1)\nu$$

whence ν may be found.

θ is the temperature of the cold ends l' and l''' of the capillary as well as the temperature at which the wet air in the burette is measured. It is determined by submerging a thermometer in the trough $M\,M$.

θ'' is the temperature of the hot part l'' of the platinum tube. Remarks concerning its measurement will be found with each table since this variable is the difficult one to evaluate correctly. The measurement of the actual value of θ'' is directly dependent on the degree of constant temperature in the helix.

R, finally, denotes the radius of the capillary tubes. It is this quantity which, in case of fine *opaque* capillary tubes, it is exceedingly difficult to determine. In some of the experiments below I subsequently filled the tubes with mercury in ways there to be indicated, and weighed the thread. But in the experiment, Tables 81 to 89, I did not wish to endanger the platinum tubes by employing this method. Nor did I think it safe to apply volumetric methods like those described on pp. 195, 214. The only procedure left therefore consists in weighing (mass m) known lengths, L, of the capillary, and measuring the external diameter R_{ex} by screw calipers. From the known density δ of platinum the internal radius R may be calculated at once in its square value as

$$R^2=R_{ex}^2-\frac{m}{\pi L\delta}$$

Unfortunately this is a crude method at best, and the problem is even more seriously difficult, because formula 6 calls for the fourth power of R.

Hence the absolute values of η'' and η in the table are distorted; but since this distortion is *uniform* for all data, and since it does not therefore affect the relative values, the errors introduced by incorrect R do not interfere with the chief purposes of the present investigation.

The attempt to obtain absolute values from metallic capillary tubes is perhaps futile. It is impossible to guaranty that in such tubes the radius is either rigorously uniform throughout the length of the tube or that the capillary canal is truly circular in section. Coiling of tubes, so essential in very high temperature work, also flattens the section. In drawing tubes flaws or splinters of metal partially projecting into the capillary canal can not always be obviated. But all these effects are not hurtful where relative results are alone of interest. This is, of course, the case in pyrometry.

Hydrogen and air, as used in the following tables, are not intended to refer to absolutely pure gases. Both gases were dried, of course, in the usual way. But the hydrogen may contain traces of air or sulphide, and the air was not freed from carbonic acid. My object in the following experiments was to test the possibility of an *identity of law in the case of two thoroughly different gases*, the zero properties of each of which were continually redetermined, i. e., before each experiment. Inasmuch as these gases are to be true gases, all vaporous constituents were to be excluded. At high temperatures, however, even this precaution is not essential.

Data.—Tables 81 and 82 contain the results of consecutive series of experiments made with air and with hydrogen, respectively. In these early experiments I did not venture to *solder* the terminals of the helix into the walls of the pneumatic trough from fear of injury to the tubes. Hence the trough leaked at high temperatures, and the water wetting the outside of the asbestus chimney or furnace which surrounds the helix and burner was the cause of an irregular distribution of temperature, which I did not foresee. Temperature being measured in the inside of the helix at a point nearest the trough is therefore decidedly low, for it is here that the effect of cooling the environment is seriously felt. The position of the thermocouple (No. 37, calibrated above) is nearly that given in Fig. 47. Moreover, the helix itself is naked, that is, not jacketed by an envelope of mica or other substance of low thermal conductivity. Temperatures near 1,000° are obtained by direct exposure to the flame of the chimneyed Bunsen burner; higher temperatures (usually above 1,200°) by exposure to the flame of the air-blast lamp. Temperatures below 800° (usually) are obtained in the air bath of the petroleum Argand burner, the chimney of which is suitably jacketed.

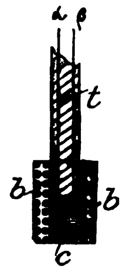

FIG. 47. Vertical section through helix. Scale ¼.

TABLE 81.—*Viscosity of air. Platinum capillary. Thermo-couple No. 37.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l''=4.4^{cm}$. $\eta_0=0.0002508$. $\theta=6°$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
124.28	76.02	165	49.11	6	0.0002592	....
124.28	76.02	162	48.95	6	2553	....
124.28	76.02	160	48.25	6	2558	....
88.49	75.92	770	47.91	6	0.0002618	....
88.49	75.92	810	50.27	6	2625	....
88.49	75.92	795	50.39	6	2570	....
88.69	75.92	810	51.34	6	2615	....
124.66	75.92	155	47.28	6	0.0002557	....
124.68	75.92	160	48.20	6	2585	....
124.76	75.92	160	48.50	6	2580	....
124.83	75.92	160	48.50	6	2584	....
124.51	75.95	725	48.43	430	0.0005255	2.096
124.64	75.95	725	47.73	442	5265	2.100
124.64	75.95	760	49.11	455	5276	2.105
124.64	75.95	760	48.11	464	5324	2.123
124.63	75.95	780	48.39	472	5370	2.142
124.61	75.95	785	47.59	483	5425	2.164
124.61	75.95	810	48.44	490	5463	2.179
124.77	75.95	935	49.85	558	0.0005670	2.262
124.84	75.95	905	48.53	554	5674	2.263
124.87	75.95	900	48.49	552	5664	2.259
124.51	75.95	905	48.58	546	5669	2.261
124.55	75.95	900	48.44	545	5665	2.259
124.55	75.95	1485	49.74	840	0.0006824	2.722
124.73	75.95	1470	49.64	828	6869	2.740
124.28	76.19	1655	50.16	880	0.0007221	2.879
124.00	76.19	1560	47.66	871	7163	2.856
124.01	76.19	1620	49.91	861	7162	2.855
124.01	76.19	1590	48.56	865	7201	2.871
124.03	76.19	2080	47.67	1141	0.0007829	3.122
124.03	76.19	2110	48.08	1136	7903	3.151
124.77	76.39	2050	48.56	1127	0.0007771	3.099
124.77	76.39	2070	49.16	1125	7765	3.096
124.77	76.39	2085	50.04	1114	7732	3.083
124.77	76.39	2040	49.30	1104	7802	3.111
124.53	76.29	160	48.75	6	0.0002546	....
124.53	76.29	160	48.71	6	2548	....
124.53	76.29	160	48.65	6	2551	....
124.53	76.29	160	48.71	6	2548	....
88.25	76.29	840	50.49	6	0.0002619	....
88.31	76.29	840	50.60	6	2627	....
88.31	76.29	840	50.60	6	2627	....
88.29	76.29	840	50.49	6	2628	....

TABLE 82.—*Viscosity of hydrogen.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0001392$. $\theta=7°$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
124.96	76.72	90	49.43	6	0.0001419	....
124.96	76.72	90	49.47	6	1418	....
124.96	76.72	90	49.49	6	1418	....
88.72	76.72	480	50.93	6	0.0001497	....
88.71	76.72	485	51.58	6	1478	....
88.73	76.72	480	51.30	6	1488	....
88.75	76.72	450	48.06	6	1491	....
124.61	76.72	90	49.34	6	0.0001409	....
124.62	76.72	90	49.56	6	1403	....
124.62	76.72	90	49.60	6	1402	....
124.61	76.72	90	49.51	6	1404	....
88.56	76.72	480	50.78	6	0.0001481	....
88.60	76.72	460	49.15	6	1472	....
88.62	76.72	480	51.39	6	1470	....
124.53	76.71	365	49.73	392	0.0002749	1.975
124.54	76.71	360	48.62	380	2747	1.974
124.58	76.71	360	43.37	428	2874	2.065
Fresh hydrogen supplied.						
125.49	77.29	380	49.99	398	0.0002792	2.006
125.53	77.29	385	49.40	411	2810	2.019
125.53	77.29	395	49.65	424	2822	2.028
125.52	77.20	420	50.51	437	2899	2.083
125.55	77.29	420	49.49	452	2905	2.087
125.63	77.29	420	48.59	461	2932	2.107
125.69	77.29	440	49.52	474	2968	2.133
126.71	77.29	530	50.26	565	0.0003251	2.336
126.55	77.29	565	48.80	634	3300	2.371
126.67	77.29	570	48.22	644	3293	2.366
126.67	77.29	600	49.69	658	3470	2.493
126.68	77.29	600	48.12	668	3446	2.476
126.70	77.29	780	48.40	848	0.0003807	2.735
126.70	77.29	780	49.19	834	3766	2.706
126.69	77.29	780	48.89	835	3786	2.720
126.70	77.29	780	48.89	834	3791	2.723
126.68	77.29	815	50.92	834	3790	2.730
126.53	77.26	1050	48.91	1006	0.0004438	3.189
126.57	77.26	1035	48.98	997	4404	3.165
126.64	77.26	1020	48.86	994	4365	3.136
Immediately after the high-temperature measurement.						
120.32	77.26	90	50.69	7	0.0001415	....
126.32	77.26	89	50.19	7	1414	....
After a day. Fresh hydrogen supplied.						
125.35	77.43	90	48.98	7	0.0001424	....
125.40	77.43	90	49.02	7	1425	....
Fresh hydrogen supplied.						
125.02	77.43	90	48.56	7	0.0001425	....
125.02	77.43	90	48.45	7	1428	....
125.03	77.43	90	48.49	7	1427	....
125.06	77.43	90	48.52	7	1427	....

TABLE 82—*Viscosity of hydrogen*—Continued.

P	p	t''	V_0	θ''	$\frac{\eta}{1+4\zeta''/R''}$	$F(\theta'')$
125.07	77.43	90	48.52	7	1428	....
89.43	77.43	480	48.56	7	0.0001579	....
89.41	77.43	480	48.62	7	1574	....
89.42	77.43	480	48.98	7	1564	....

Bearing in mind therefore that the curve

$$F(\theta'')=\frac{\dfrac{\eta''}{1+4\dfrac{\zeta''}{R''}}}{\dfrac{\eta}{1+4\dfrac{\zeta}{R}}}$$

as given by these results, is necessarily high, I constructed $F(\theta'')$ both for Table 81 and for Table 82. The result shows a most surprising degree of coincidence in the values for air and for hydrogen, proving beyond a doubt that the same law of variation $F(\theta'')$ must apply to both gases. Since the locus constructed falls below $(1+\alpha\theta'')^{\frac{3}{4}}$, where $\alpha=0.003665$, the coefficient of expansion of gases, the true value of $F(\theta'')$ must fall decidedly below $(1+\alpha\theta'')^{\frac{3}{4}}$ and *a fortiori* below the formula

$$\frac{\eta''}{\eta_0}=1+0.002751t-0.00000034t^2$$

by which Holman reproduced the data of his fine observations for air between 0° C. and 100°. Now, although the data in the locus drawn fall below $(1+\alpha\theta'')^{\frac{3}{4}}$, it can not at once be assumed that $(1+\alpha\theta'')^{\frac{3}{4}}$ is to be discarded as the value of $\frac{\eta''}{\eta_0}$; for in view of the occurrence of the factor

$$\frac{1+4\dfrac{\zeta}{R}}{1+4\dfrac{\zeta''}{R''}},$$

where ζ is essentially positive and increasing with θ'', it does not follow that $F(\theta'')$ and $\frac{\eta''}{\eta_0}$ are identical.

The curve shows the effect of a cold environment in a very striking way; for the Bunsen-burner temperatures here lie at only 850°, and 1,140° is the highest temperature reached by the blast-lamp. Clearly the mean temperature of the thermo-couple is only a nominal value for the mean temperature of the helix of platinum tube. This is proved by the high values of $F(\theta'')$ for hydrogen at 1,000°; for these large data are due to the fact that platinum is pervious to hydrogen, an effect which, in the following tables, does not produce a serious discrepancy until much higher temperatures are reached.

In Tables 83 and 84 results are given for hydrogen and air, respectively, with an improved form of apparatus. The thermo electric junction still occupies a position near the center of figure of the helix and protected from direct action of the flame by a flat plug or pellicle of asbestus (Fig. 47*c*); but the terminal tubes of the helix are soldered into the walls of the pneumatic trough, through which they project. In this way a leakage of water is prevented, and the chimney of the burner remains dry and of unifrom temperature. The helix, however, is naked here, as in the foregoing experiment.

TABLE 83.—*Viscosity of hydrogen.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0001416$. $\theta=6_0$ R = 0.00794^{cm}.]

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
123.97	75.66	95	51.38	6	0.0001427	....
123.97	75.66	90	48.73	6	1426	....
123.97	75.66	90	48.70	6	1427	....
123.97	75.66	90	48.80	6	1424	....
123.98	76.66	90	48.78	6	1425	....
123.82	75.66	90	48.33	6	0.0001432	....
123.83	75.66	90	48.37	6	1431	....
123.81	75.66	90	48.42	6	1429	....
123.83	75.66	90	48.37	6	1431	....
123.85	75.66	90	48.39	6	1431	....
123.83	75.66	90	48.37	6	1431	....
123.88	75.60	440	50.04	482	0.0002813	1.986
123.90	75.60	440	49.83	490	2831	1.999
123.92	75.60	440	49.64	490	2842	2.007
123.92	75.60	410	49.61	504	2867	2.021
123.92	75.60	440	47.89	511	2874	2.030
123.67	75.62	630	50.63	671	0.0003244	2.291
123.68	75.62	660	50.96	695	3307	2.336
123.64	75.62	660	50.23	705	3320	2.345
123.64	75.62	....	50.93	715	....	....
....	75.62	680	....	....	0.0003340	2.359
123.85	75.62	660	51.75	688	3295	2.327
123.85	75.62	660	51.55	691	3299	2.330
123.85	75.62	660	50.95	700	3306	2.335
123.85	....	660	50.14	707	3336	2.356
121.75	75.72	1115	50.82	985	0.0004162	2.939
121.73	75.72	1115	50.77	985	4165	2.941
124.64	76.25	1080	50.82	1010	0.0004231	2.987
124.63	76.25	1080	50.73	1010	4237	2.992
124.81	76.25	1080	51.10	1007	4237	2.902
124.83	76.25	1080	51.19	1005	4238	2.993
124.84	76.25	1080	51.21	1006	4234	2.900
124.65	76.32	1560	51.24	1222	0.0005254	3.710
124.64	76.32	1560	51.26	1227	5189	3.664
124.65	76.32	1560	51.45	1224	5228	3.692
124.79	76.32	1560	52.23	1223	5176	3.655

TABLE 83.—*Viscosity of hydrogen*—Continued.

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
124.31	76.35	90	47.52	5	0.0001464	....
124.31	76.35	95	50.56	5	1453	....
124.31	76.35	95	50.85	5	1444	....
124.31	76.35	95	50.96	5	1441	....
124.31	76.35	95	50.96	5	1441	....
123.99	76.37	95	50.51	5	0.0001441	....
123.99	76.37	95	50.50	5	1442	....
124.03	76.37	95	50.47	5	1444	....
124.00	76.37	95	50.51	5	1442	....

TABLE 84.—*Viscosity of air.*

[Capillary tube No. 10. $L = 33.43^{cm}$. $l'+l''' = 4.4^{cm}$. $\eta_0 = 0.0002472$. $\theta = 5°$. $R = 0.00794^{cm}$.]

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
125.24	77.08	165	51.31	5	0.0002517	....
125.24	77.08	165	51.31	5	2517	....
125.23	77.08	165	51.36	5	2514	....
125.23	77.08	165	51.46	5	2509	....
125.25	77.08	165	51.36	5	2515	....
125.36	77.08	165	51.52	5	2514	....
125.08	77.08	165	51.16	5	0.0002514	....
125.08	77.08	165	51.16	5	2514	....
125.08	77.08	165	51.22	5	2511	....
125.08	77.08	165	51.22	5	2511	....
124.93	76.97	560	50.77	335	0.0004385	1.774
124.93	76.97	780	51.90	473	4925	1.993
124.95	76.97	740	52.20	448	4805	1.944
124.77	76.80	810	51.83	491	0.0005035	2.037
124.77	76.80	810	51.11	499	5050	2.043
124.74	76.80	880	51.57	536	5201	2.104
124.73	76.80	920	51.43	563	5285	2.138
124.73	76.80	945	51.67	575	5331	2.157
124.77	76.80	960	51.57	585	5377	2.175
124.76	76.80	980	51.94	595	5391	2.181
124.04	76.19	1680	50.62	930	0.0006910	2.796
124.08	76.17	1665	51.42	917	6836	2.766
124.05	76.13	1665	50.98	919	6882	2.784
123.97	76.05	1665	51.15	914	6883	2.785
123.88	75.97	1665	51.61	912	6822	2.760
123.69	75.79	2780	51.21	1337	0.0008598	3.479
123.65	75.71	2820	50.87	1337	8784	3.554
123.64	75.66	2860	50.81	1337	8925	3.611
123.60	75.62	2880	50.85	1340	8966	3.627
123.37	75.97	165	50.10	5	0.0002500	....
123.37	75.97	165	49.99	5	2505	....
123.37	75.97	165	50.15	5	2498	....
123.40	75.97	165	50.03	5	2505	....
123.40	75.97	165	50.09	5	2503	....

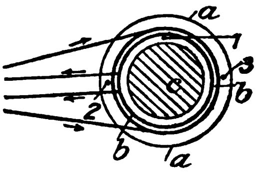

FIG. 47a. Plan of helix and thermo-couples.

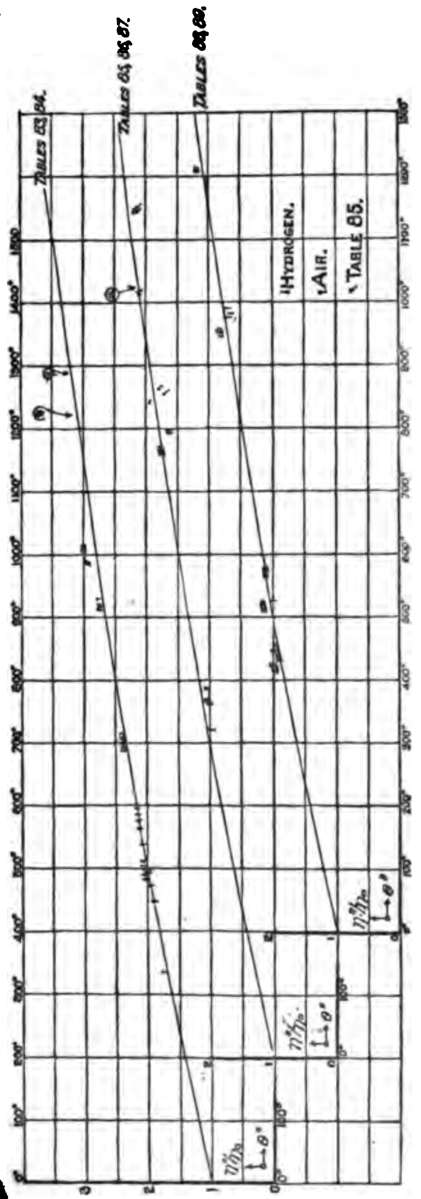

FIG. 48. Chart showing viscosity as a function of temperature.

These results (Tables 83 and 84) justify the predictions made relative to the hurtful character of the leak. For if $F(\theta'')$ be constructed it falls decidedly below the earlier curve. Below 1,000°, moreover, the air and hydrogen loci show a striking degree of coincidence (see chart, Fig. 48), substantiating the earlier inference that $F(\theta'')$ has the same value for these two gases, and that the value of θ'', thermo-electrically measured, is not the true mean temperature at which transpiration actually occurs. Above 1,000° the air and hydrogen curves diverge; but this is due to the fact that platinum is much more *pervious* to hydrogen than to air. Again, in consequence of the tendency of the gases of the burner to enter the tubes, as well as the relatively large negative errors of θ'' at high temperatures, the curvature of both loci changes from concavity downwards below 1,000° to concavity upwards above 1,000°. Hence above 1,000° the true character of η''/η_0 is marred by the occurrence of diffusion across the walls of the platinum capillary tube. It appears from the data, at extremes of high temperature (hydrogen $\theta=1,225°$ nearly, air $\theta=1,335°$ nearly), that the large distortion produced by diffusion is nevertheless of a determinable kind. It may therefore be eliminated by applying suitable corrections, as will be stated below. The occurrence of the consecutive high-temperature points, lying nearly vertically one above another, is due to the fact that the non-registered temperature at the *outside* of the helix continues to increase long after the internal and registered temperature is practically stationary. The mean temperature of the helix is thus still on the increase, after the temperature of the thermo-couple is constant, and the discrepancy in question points out an ordinary phenomenon of heat conduction. All these peculiarities appear clearly in Fig. 48, where points dashed upward refer to hydrogen, points dashed downward refer to air. Leaving the exceptional values out of consideration, the data of these tables are of special importance. They show that the locus $F(\theta'')$ does not only lie below $(1+\alpha\ \theta'')^{\frac{3}{4}}$, but that its value is most probably $(1+\alpha\,\theta'')^{\frac{2}{3}}$. Indeed, the close coincidence of the data between 400° and 800° with the function $(1+\alpha\,\theta'')^{\frac{2}{3}}$ is an exceedingly striking observation. When it is called to mind that theoretical reasons suggest the exponential form $(1+\alpha\ \theta'')^{n}$, that the effect of slip $1+4\,\frac{\zeta}{R}$ is in the opposite sense to the necessarily negative error in θ'', then the acceptation of $(1+\alpha\,\theta'')^{\frac{2}{3}}$ as the simplest convenient expression for the co-ordination of all the data $F(\theta'')$ is easily justified.

Tables 81 to 84 have proved beyond a doubt that the predominating error in the present experiment is introduced by the fact that the mean temperatures of the viscosity pyrometer and of the thermo-element are essentially different. The degree of constant temperature throughout the space occupied by these two instruments is therefore by no means sufficient; hence I made a few measurements on the effect produced by changing the position of the thermo-couple and of enveloping the helix with layers of a non-conducting material. I also endeavored to test in how far a more reliable temperature datum could be obtained from the simultaneous indications of two or more thermo-couples touching different points on the inside and on the outside of the helix.

TABLE 85.—*Viscosity of air. Miscellaneous tests.*

[Capillary tube No. 10. $L=33.48^{cm}$. $l'+l'''=4.4^{cm}$ $\eta_0=0.0002472$. $\theta=6°$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta/R}$	$F(\theta'')$
I.—Thermo-couple nearly naked.						
123.11	75.93	170	51.35	5	0.0002497	....
123.13	75.93	170	51.35	5	2499	....
123.15	75.93	170	51.40	5	2497	....
123.17	75.93	170	51.38	5	2500	....
123.17	75.93	170	51.38	5	2500	....
124.29	75.80	1800	51.60	1055	0.0006716	2.717
124.31	75.80	1950	51.60	1040	7359	2.977
124.30	75.80	1845	51.00	1062	6933	2.805
124.17	75.89	2460	50.96	1347	0.0007684	3.109
124.22	75.82	2460	50.50	1338	7813	3.161
124.27	75.79	2460	50.39	1336	7852	3.177

TABLE 85.—*Viscosity of air. Miscellaneous tests*—Continued.

P	p	t''	V_0	θ''	$\frac{\eta''}{1+4\zeta/R}$	$F(\theta'')$
II.—Two thermo-couples touching the inner face of the naked helix.						
125.30	76.95	165	51.38	6	0.0002514	....
125.29	76.95	165	51.38	6	2513	....
125.29	76.95	165	51.35	6	2514	....
125.31	76.95	165	51.45	6	2511	....
125.40	76.95	165	51.68	6	2506	....
124.97	76.89	1780	52.74	964	0.0006947	2.811
124.95	76.84	1740	51.69	962	6942	2.809
124.89	76.80	1770	52.47	959	6966	2.819
124.85	76.76	1740	52.05	956	6917	2.789
124.75	76.66	2520	51.30	1224	0.0008453	3.420
124.78	76.62	2580	51.31	1227	8594	3.477
124.92	76.59	2700	51.51	1231	9028	3.653
III.—Temperature measured inside and (by contact) outside.						
124.71	76.61	2940	51.50	1380 1233	0.0009340	3.778
124.67	76.58	1800	51.38	1132 988	0.0006677	2.702
124.70	76.60	1800	51.07	1035 974	0.0007021	2.841

In the first part of Table 85 the couple is inserted into the helix, with its junction near the base, so as to be played upon directly by the flame of the burner. The temperatures so obtained fluctuate in value over so large an interval that it is difficult to get a fair mean value. This appears from the wide distribution of the points obtained on the curve. Their mean position, however, is unmistakably below $(1+\alpha\,\theta'')^{\frac{2}{3}}$, a result consistent with the results of the foregoing tables, inasmuch as the error of $F(\theta'')$ is here positive, because the error of θ'' is positive. The helix in these experiments was naked.

In the second part of Table 85 two thermo-couples are inserted touching the inner face of the helix, with their junction at points respectively nearest to and farthest from the walls of the trough. The results indicate a series of points at 960°, which are nearer the curves than before, whereas the results at 1,230° are abnormally high. Comparing the temperatures at the two points of the internal face, I found $\theta_1''=1{,}255°$ and $\theta_2''=1{,}235°$, so that even at the temperatures of the blast-lamp the differences of temperature for points on the inner face of the helix are not of serious magnitude. The discrepancy must therefore be looked for in thermal differences between the inside and outside faces of the helix.

In the third part of Table 85 measurements of the kind just specified are given. The two figures under θ'' are thermal data for the inside and outside faces of the helix, the latter being obtained by touching the surface with the junction of a thermo couple. The discrepancies thus obtained are alarmingly large (150°); and although this datum can be only a superior limit for the discrepancy in question, it nevertheless points emphatically to the necessity of resorting to better means of insuring constancy of temperature throughout the space occupied by the two pyrometers. The final values of $F(\theta'')$ in this table are again abnormally large, so as to suggest that some vitiating error escaped detection. Comparing the thermo-couple which had been used in all these experiments with a fresh couple, I found mean values for the temperature of the Argand air bath, $\theta_1=822^{\circ}$ and $\theta_2''=804^{c}$, so that the result of repeated and prolonged firing can not have exceeded 20°.

The irregular results of Table 85 show the importance of jacketing the helix with non-conducting material, and of using at least three thermo-couples for the evaluation of θ''. One thermo-couple on the inner face is sufficient, but at least two are necessary to measure temperature at the external face.

In Tables 86 to 89 the external face of the helix is enveloped by a layer of mica, pressed against the surface by platinum wires, drawn tensely around the mica. In Fig. 47*a* the helix of platinum capillary tube is shown at *b*, the surrounding envelope of mica at *a*. The junctions of the thermo-couples placed at 1, on the inner face of the helix, pressed against it by a plug of asbestus, *c*, and at 2 and 3 between the outer face of the helix and the mica envelope. Junctions 2 and 3 are pressed against the helix by the external platinum wiring, which holds the mica jacket in place. Fine plates of mica insulate the ends of the thermo-couples from the helix above it. The stem insulators described on page 95 are of service in keeping the wires apart. In the tables, θ_1'' denotes the temperature at the internal, θ_2'' the mean temperature of the external face. To secure identity in the thermo-electric indications the old junctions were cut off and new junctions were fused for each of the couples, Nos. 37, 38, 39, used in the measurement. The calibration of these was effected above, Chapter IV.

TABLE 86.—*Viscosity of air.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0002491$. $\theta=7^{\circ}$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ_1''	θ_2''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
124.00	76.08	165	49.95	7	7	0.0002526	....
124.00	76.08	165	49.83	7	7	2532	....
124.00	76.08	165	49.84	7	7	2532	....
124.00	76.08	165	49.94	7	7	2527	....
124.01	76.08	165	49.94	7	7	2528	....
123.51	75.92	1750	51.85	984	1007	0.0006693	2.687
123.45	75.87	1760	51.90	983	1004	6666	2.676
123.38	75.81	1740	51.36	984	1004	6654	2.671

TABLE 86.—*Viscosity of air*—Continued.

P	p	t''	V_0	θ_1	θ_2	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
123.32	75.75	2339	51.05	1200	1224	0.0007757	3.114
123.29	75.72	2340	50.48	1204	1230	7820	3.139
123.25	75.67	2340	50.76	1204	1233	7765	3.117
123.39	75.68	860	52.69	515	525	0.0004977	1.998
123.65	75.68	890	50.91	557	567	5114	2.053
123.61	75.68	910	51.00	557	578	5068	2.082
123.58	75.68	930	50.79	580	592	5210	2.091
123.61	75.68	960	51.37	592	604	5254	2.109
123.36	74.73	165	49.59	8	8	0.0002547	....
123.37	74.73	165	49.59	8	8	2547	....
123.36	74.73	165	49.50	8	8	2552	....
123.36	74.73	165	49.59	8	8	2547	....
123.33	74.73	165	49.63	8	8	2543	....

TABLE 87.—*Viscosity of hydrogen.*

[Capillary tube No 10. $L=33.43^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0001294$. $\theta=8^0$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ_1''	θ_2''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
122.48	74.71	90	50.66	8	8	0.0001330	....
122.49	74.71	88	49.81	8	8	1323	....
122.50	74.71	88	49.79	8	8	1324	....
122.50	74.71	88	49.69	8	8	1326	....
122.50	74.71	88	49.68	8	8	1327	....
122.20	74.62	88	49.51	8	8	0.0001323	....
122.22	74.62	88	49.51	8	8	1324	....
122.24	74.62	88	49.55	8	8	1324	....
122.22	74.62	88	49.62	8	8	1320	....
122.24	74.62	88	49.58	8	8	1323	....
122.30	74.69	885	50.11	947	970	0.0003525	2.725
122.30	74.73	870	49.10	948	972	3528	2.726
122.32	74.75	870	49.02	948	976	3529	2.727
122.36	74.81	875	49.25	946	978	3533	2.731
122.43	74.86	900	49.68	955	984	3584	2.770
122.97	74.93	1340	49.64	1196	1228	0.0004588	3.546
122.94	74.96	1350	49.96	1202	1228	4577	3.538
122.96	74.99	1350	50.39	1192	1226	4556	3.521
124.56	76.86	495	51.65	526	538	0.0002924	2.260
124.56	76.86	495	51.09	531	544	2939	2.271
124.56	76.86	495	50.83	535	547	2939	2.271
124.54	76.86	495	50.48	536	552	2952	2.281
124.56	76.86	495	50.18	541	554	2960	2.287
124.58	76.86	495	50.09	544	556	2957	2.285
125.09	77.08	85	50.28	8	8	0.0001304	....
125.08	77.08	85	50.28	8	8	1304	....
125.09	77.08	85	50.30	8	8	1304	....
125.08	77.08	85	50.28	8	8	1304	....
125.09	77.08	85	50.28	8	8	1304	....

TABLE 88.—*Viscosity of hydrogen.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0001294$. $\theta=7°$. $R=0.00794^{cm}$.]

P	p	t''	V_0	θ_1''	θ_2''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
123.30	76.95	90	50.00	7	7	0.0001332	....
123.32	76.95	90	50.00	7	7	1333	....
123.31	76.95	90	50.00	7	7	1333	....
155.27	76.55	360	50.82	410	418	0.0002518	1.946
155.27	76.55	360	50.42	412	420	2529	1.954
155.27	76.55	360	50.02	416	425	2536	1.960
155.30	76.55	360	49.67	420	426	2547	1.968
155.30	76.55	440	50.89	504	510	0.0002741	2.118
155.27	76.55	450	51.37	509	516	2747	2.123
155.25	76.55	450	51.23	512	519	2747	2.124
155.45	76.59	450	50.87	514	522	0.0002762	2.135
155.35	76.59	450	50.57	516	525	2770	2.141
155.45	76.59	450	50.63	517	526	2766	2.138
156.10	76.67	890	50.89	954	956	0.0003635	2.809
156.07	76.67	890	51.00	954	953	3629	2.805
156.05	76.67	890	51.43	952	951	3606	2.787
156.07	76.67	870	50.01	946	946	3601	2.783

TABLE 89.—*Viscosity of air.*

[Capillary tube No. 10. $L=33.24^{cm}$. $l'+l'''=4.4^{cm}$. $\eta_0=0.0002491$. $\theta=8°$. $R=0.0794^{cm}$.]

P	p	t''	V_0	θ_1''	θ_2''	$\frac{\eta''}{1+4\zeta''/R''}$	$F(\theta'')$
125.50	77.01	165	50.72	7	7	0.0002579	....
125.51	77.01	165	50.75	7	7	2579	....
125.53	77.01	165	50.72	7	7	2581	....
124.71	76.87	710	51.10	424	436	0.0004820	1.935
124.71	76.87	710	50.22	430	443	4865	1.953
124.69	76.87	735	51.03	439	453	4995	2.005
124.65	76.87	750	50.93	449	462	4937	1.982
124.73	76.87	930	51.34	558	568	0.0005351	2.148
124.68	76.87	930	50.98	562	574	5351	2.148
124.68	76.87	940	51.34	565	576	5360	2.152
124.68	76.87	940	50.93	569	580	5364	2.153
124.95	76.89	1710	51.42	964	987	0.0006784	2.723
124.95	76.89	1715	51.20	970	992	6645	2.668
124.95	76.89	1740	51.25	979	1000	6842	2.747
124.96	76.98	2370	51.27	1206	1214	0.0008013	3.217
124.96	76.98	2370	51.17	1207	1214	8028	3.223
124.95	76.98	2370	51.25	1207	1210	8017	3.218

The results in Table 86 justify the predictions made. Compared amongst themselves the values are excellent. Below 1,000° the data lie below the function $(1+a\theta'')^{\frac{1}{2}}$, whereas the extreme points (1,215°)

coincide with $(1+\alpha\theta'')^{\frac{2}{3}}$ almost perfectly. In general therefore the results of earlier investigations (Table 81–85) are emphatically corroborated. Having finished the measurements for air, I passed hydrogen through the same apparatus. The results, near 1,000° (Table 87), coincide almost perfectly with the curve $(1+\alpha\theta'')^{\frac{2}{3}}$. The results above 1,200° are abnormally high, because platinum is pervious to hydrogen. I was not a little surprised therefore on finding the results at 500°, although very good when compared amongst themselves, much too large to accord with the other data. The error is larger than can be referred to anything short of an undiscovered accident. I suspect the hydrogen of these experiments in some unforeseen way to have been contaminated with either air or moisture, since the error is constant for all the observations.

Not being able to discover the cause of the discrepancy, however, I resolved to repeat the work with the apparatus adjusted anew. These results are given in Table 88. The results agree much more closely with the exponential $(1+\alpha\theta'')^{\frac{2}{3}}$, showing the corresponding data of the former series in error. The somewhat high values of $F(\theta'')$ are the result of the low value of η_0, to which these data are referred. The difficulties met with in operating with hydrogen induced me to investigate another series for air, which series is given in the last table, 89. The results fall slightly above $(1+\alpha\theta'')^{\frac{2}{3}}$ at 500°; slightly below the exponential at 1,000°; above it at 1,200°; but the accordance throughout is satisfactory. (See Fig. 48.)

The large number of data for θ_1 and θ_2, which the Tables 86–89 contain, show that the thermal discrepancy has been reduced to low limits, and that its effect is apt to be relatively large in case of low values of θ. To properly jacket the helix is a practical problem of great difficulty, because accidental bending or twisting of the thin capillary tube is apt to produce fine longitudinal fissures, or variations of bore, or to introduce other sources of uncertainty or error. Mica insulations become friable and can not be thoroughly relied upon after prolonged heating. Hence all the manipulations must be effected with great care, and therefore consume much time. For these reasons I believe that to improve the results further it will be expedient to introduce a radical change of method, such as I will describe below.

As a whole, the above tables conclusively indicate that many residual errors are the result of variations in the composition of the gases. Hence, before proceeding to a general discussion of the above data, I shall insert a tabular view of the successive values of the viscosity of the gases at zero degrees centigrade. This is given in Table 90, in which the temperatures θ, at which the quantities

$$\frac{\eta}{1+4\frac{\zeta}{R}}$$

were found, are inserted, as well as the corresponding values of

$$\frac{\eta_0}{1+4\frac{\zeta_0}{R_0}}$$

computed for them by using Holman's equation,

$$\frac{\eta'}{\eta_0}=1+0.002751\theta-0.00000034\theta^2.$$

I also insert the pressure P, at which the gas enters the platinum capillary.

TABLE 90.—*Successive values of* η_0.

Gas.	Date.	θ	$\frac{\eta}{1+4\frac{\zeta}{R}}\times 10^6$	$\frac{\eta_0}{1+4\frac{\zeta}{R}}\times 10^6$	P	Mean $\eta_0 \times 10^6$
H_2....	March 26	7°	133.3	130.8	123.3	
H_2....	March 23	8	130.4	127.5	125.1	
H_2....	March 21	8	132.3	129.4	122.2	
H_2....	March 20	8	132.6	129.7	122.5	
Air...	March 26	7	254.8	250.0	125.5	
Air ..	March 20	8	254.7	249.2	123.4	H_2... 129.4
Air...	...do	7	252.9	248.1	124.0	Air... 249.1
Air...	March 19	6	251.2	247.2	125.3	
Air...	March 18	5	250.0	246.5	123.1	
Air...	...do	5	250.2	246.7	123.4	
Air...	March 15	5	251.4	247.9	125.2	
Air...	...do	5	251.2	247.7	125.1	Air... 247.2
H_2...	March 14	5	144.9	142.9	124.3	
H_2....	.. do	5	144.2	142.2	124.0	
H_2....	March 13	6	142.6	140.4	124.0	
H_2....	...do	6	143.1	140.9	123.8	H_2... 141.6
H_2....	March 10	7	142.7	140.0	125.0	
H_2....	...do	7	142.5	139.8	125.4	
H_2....	March 9	7	141.5	138.8	126.3	H_2... 139.5
H_2....	March 8	6	141.8	139.6	125.0	
H_2....	...do	6	141.8	146.4	88.7	
H_2....	...do	6	140.4	138.2	124.6	(H_2... 146.0)
H_2....	...do	6	147.8	145.6	88.6	H_2... 138.9
Air...	March 7	6	254.8	250.8	124.5	
Air...	...do	6	262.5	258.5	88.3	Air... 250.8
Air...	March 3	6	255.5	251.5	124.2	
Air...	...do	6	260.7	256.5	88.5	(Air... 256.5)
Air...	...do	6	257.7	253.5	124.7	Air... 252.5

DISCUSSION.

Viscosity at zero.—It is expedient to begin this paragraph with an examination of the consecutive values of the zero-viscosity η_0 of the several gases, since the constant η_0 must enter fundamentally into all the inferences to be drawn. Turning to Table 90, on page 271, the singularly high values there incorporated at once strike the eye. The clue to these large discrepancies is, however, at hand; for

$$\eta = \frac{\pi\left(1+\frac{\zeta}{R}\right)}{16}\,\frac{P^2-p^2}{p}\,\frac{t}{V}\,\frac{R^4}{L}$$

and it is therefore clear that since $\frac{\delta\eta}{\eta} = 4\,\frac{\delta R}{R}$ even slight errors in R at once produce serious effect on η. I have stated that because of the difficulty encountered in constructing the capillary apparatus faultlessly, I did not wish to subject the tubes to any experiment which might tend to injure them; I stated also that in the discussions of the present part of the chapter absolute data were of inferior interest. Hence, without forgetting the occurrence of the uniformly large values of η here found, the question may be waived, to be resumed in the next part in connection with other relevant data. The one property of η_0 which has an important bearing on the present discussion is its degree of constancy as regards time. If the values of η_0 in Table 90 be graphically constructed as they vary with the data belonging to each, the curves resulting show that η_0 has a slight tendency to increase. Disregarding the data between March 3 and March 7, which refer to an earlier form of apparatus, it appears that in the hydrogen data between March 8 and March 14 the mean increase of η_0 is somewhat less than 0.5 per cent. per day of use; in the results for air between March 15 and March 26 less than 0.2 per cent. per day of use; in the final results for hydrogen between March 20 and 26 the results vary irregularly, and their mean ascent is zero. These data constitute an exceedingly favorable verdict relative to the pyrometric application of the principle of viscosity. They show that for large mercury pressures like 125^{cm} and 76^{cm}, respectively, at the two ends of the platinum capillary tube, no serious change of the radius of the tube need be apprehended at temperatures even as high as 1,400° (white heat). In this respect the present results are valuable. The slight tendency of η_0 to increase just mentioned, is in accordance with an increase of the capillary radius resulting from the excess of internal pressure. This follows from Meyer's equation, but whether the observed result may not be equally well explained as resulting from variations in the composition of the gases or from similar progressive causes can not be ascertained. It suffices for the present purposes that the time variations of η_0 have been found negligible, and that therefore the dimension of the platinum capillaries used in the above experiments have remained practically unchanged, when the mean excess of internal pressure at white heat was about ⅓ of an atmosphere.

The use of different gases (air, hydrogen) in these experiments was principally to vary the conditions of experiment and to detect the laws of variation with greater certainty. Hence ordinary care was taken in drying the gases, air being passed through a tube of $CaCl_2$ and hydrogen both through $CaCl_2$ and concentrated H_2SO_4. But neither was the hydrogen purified of sulphide or air or other attendant gases, nor was air purified of carbon dioxide. I desisted from these special precautions because above red heat platinum is pervious to the hydrogen gases of the Bunsen flame, so that in non-enameled platinum capillaries the purity of the transpiring gas could not be vouched for, even in the case of a gas originally pure. Again, at the temperatures (500° to 1,300°) within which my data chiefly apply slightly moist air and dry air, pure and gaseously impure hydrogen, are probably equally perfect gases. Hence there occur in my results two values for the zero-viscosity of hydrogen, $140:10^6$ and $129:10^6$, respectively, which correspond to gases taken from different gasometers at different times. The variations of η_0 for air are smaller, ranging from $247:10^6$ to $252:10^6$. The variable character of η_0 made it necessary to make the low-temperature measurement before and after each series of high-temperature measurement made. Indeed, I did not anticipate such large fluctuations in η_0, and despite the precautions taken the discrepancies here in question have produced no trifling distortions in the high-temperature results which follow. This I shall soon have occasion to show. When the gases forced through the capillaries are urged forward by an advancing surface of mercury (as in the above experiments) traces of mercury vapor will also pass along with the gas, but the tension of mercury vapor at 20° is only 0.002^{cm} to 0.004^{cm}. Hence this discrepancy is nil.

Finally, Table 90 contains values for η_0 derived both for $P=125^{cm}$ and for $P=88^{cm}$. Curiously enough, the value of η_0 for low pressures (P) is decidedly the greater, being about 5 per cent. greater for hydrogen and about 2 per cent. greater for air. This result belongs also to the discussion of the next section. Here it is sufficient to note that if measurements were made at smaller values of P than the ones customary (125^{cm}), the relative values $\frac{\eta''}{\eta_0}$ where η'' is a high-temperature viscosity, would not be larger in value than those admitted into the above tables. In other words, so far as the present evidence goes, the zero-viscosity η_0 has not been increased by the relatively large values of P (125^{cm}) employed throughout the course of the work, and hence $\frac{\eta''}{\eta_0}$ can not be too small.

Viscosity at high temperatures, kinetic inferences.—In order to proceed with the discussion of the high-temperature viscosities, Tables 83 to 89 may be consulted, the values of Tables 81 and 82 being in error in the sense already indicated. If all the values of $F(\theta'')$ be constructed as functions of θ'', the graphic representation Fig. 48 will show that the individual data group themselves in a band or pathway, of which the function $(1+\alpha\theta'')$ is so nearly the axis that it is at once justifiable to accept it as such. Hence, even if there were no ulterior reasons for accepting the given function, it is, at the present stage of investigation, a justifiable inference that the viscosity of a perfect gas varies as the $\frac{2}{3}$ power of absolute temperature. Now, inasmuch as by the relation of Maxwell

$$\eta=0.318\ \rho L\Omega,$$

where ρ is the density, Ω the velocity of the mean square, and L the mean free path of the molecule of gas, and inasmuch as $\Omega=\Omega_0\sqrt{1+\alpha\theta''}$ and L are the only variables in this equation whose values change with θ'', it follows that

$$L=L_0\sqrt[6]{1+\alpha\theta''}$$

In other words, the mean free path of the molecule of a perfect gas varies as the sixth root of absolute temperature. Moreover, in view of the equation $\Omega=\Omega_0\sqrt{1+\alpha\theta''}$, it furthermore follows that the mean free path of the molecule of a perfect gas varies as the cube root of the velocity of the mean square. This result is suggestive, perhaps; for if there be given a gas consisting of a fixed number of molecules in a fixed volume, or, in other words, if ρ be constant, then the only effect produced by varying the temperature θ'' is a mean increase of Ω distributed uniformly throughout the volume of the gas. If the change of Ω due to temperature be taken as a measure of the effect produced by temperature, as it were equally in all directions, then the part of this thermal effect apportioned to the linear magnitude L is plausibly represented by the cube root of Ω.

Again, if the equation of Clausius be considered, viz,

$$L=\frac{1}{\sqrt{2}}\frac{\lambda^3}{\pi\varsigma^2}$$

where λ^3 is the mean volume per molecule and ς the radius of Clausius's "Wirkungssphäre," then it appears that the volume inclosed within the "Wirkungsphäre" is diminished in magnitude by temperature; and that the diminution takes place proportionally to the square root of the velocity of the mean square (Ω).

$$\varsigma^3=\varsigma_0^3\frac{\sqrt{\Omega_0}}{\sqrt{\Omega}}$$

Sources of error.—Having thus stated the general character of the results of the above tables, it is necessary to find the conditions upon which their validity depends, and to inquire as fully as the present researches permit into the facts which militate against the inferences drawn. This is by no means easy, nor even fully possible on the basis of the experimental material in hand.

The principal cause of discrepancy in the present work is this, that even in the most carefully adjusted forms of the present apparatus the mean temperature registered by the thermo-couple and the mean temperature of the helix of capillary tube are not necessarily the same. Each of these pyrometers furnishes its own thermal datum correctly; but these data have reference to environments which are not thermally identical. In short, the degree of constant temperature throughout the space enveloping the helix is as yet far from satisfactory; and the residual differences of temperature between the inside and the outside of the helix or between its top and bottom surfaces have not been rigorously allowed for. To this must be added the fact that the thermo-couple was not compared with the air thermometer at temperatures above 1,300°, and that the calibration in question loses in accuracy when these high temperatures are approached. (Cf., Figs. 41 and 42.) Hence, in view of the great difficulties in the way of correct temperature measurement, it is hardly profitable to enter into more than a cursory consideration of the minor sources of error.

In addition to the extraneous causes for incorrect temperature measurement, there is also an internal cause, due to the expansion of the transpiring gas from the pressure P to the pressure p. Meyer has elaborately discussed this phenomenon. Again, the purely convective effect due to the introduction of cold gases into the capillary tube is not to be lost sight of. In experiments of the next section I found a cooling effect as high as 20°. In the present experiments, where thin tubes and slow currents alone occur, the convection error is nil.

To avoid incidental complications the radius of the capillary tubes here in question was chosen small ($R < 0.01^{\text{cm}}$), so that the Meyer formula fully applies. Again, preference is given to absolute methods of experiment; differential methods, inasmuch as they compare two magnitudes without fully characterizing either, would have encumbered the present research with an additional element of uncertainty.

Diffusion.—The observed circumflexion of the curve which represents the mean distribution of the points in the diagram, Fig. 48, at a temperature near 1,000°, together with the fact that this change of the sign of curvature is much more pronounced for hydrogen than for air, points, I think significantly, to the occurrence of diffusion of gases through the walls of the platinum capillary tube. In the case of transpiration experiments with air, the hydrogen gases of the burner passing through the platinum septum combine with the oxygen of the capillary current within. There results an increase of the volume of the oxygen combined as 1 : 2; but as the water formed is absorbed in the pneumatic apparatus, it follows that the volume V_0 actually measured by the burette is too small. Again, in the case of transpiration experiments with hydrogen the prevailing diffusion is from within outward, so that hydrogen simply leaks out of the tube. Thus the volume of V_0 actually measured is again too small. Hence in the case both of air and of hydrogen, since V_0 is negatively in error, the error of η'', which varies inversely as V_0, will be positive. This accounts for the circumflexion discrepancy in question, or at least for the difference of behavior of hydrogen and air.

A final remark relative to the surface disintegration (Zerstäubung) of red hot platinum, as observed by Nahrwold[1], Berliner[2], Kayser[3], and others, must be made here. Unfortunately my work was too far advanced when this phenomenon[4] was being discussed to permit me to make special investigations with reference to it; nor do I now see how allowance for the phenomenon is to be made. I do not believe that the error thus left unaccounted for is of a serious kind. For instance, in Nahrwold's[5] last paper it is shown that metallic particles fly off from red hot platinum much less easily in hydrogen than in air.[6] In case of both gases, however, the thermal relations of viscosity are subject to the same law. Hence the discrepancy due to surface disintegration is probably nil. 1889.

Sliding coefficient.—To return to the formula selected on page 273, it appears from the remarks there made that the full form in which it applies to transpiration work must be

$$\frac{\eta''}{1+4\frac{\zeta_0}{R_0}\frac{\sqrt[6]{1+\alpha\theta''}}{1+\beta\theta''}}=\frac{\eta_0}{1+4\frac{\zeta_0}{R_0}}(1+\alpha\theta'')^{\frac{2}{3}}$$

where R_0 is the zero radius and β the mean coefficient of expansion of the platinum capillary through which transpiration takes place. This formula follows at once for the law accepted above ($\eta''=\eta_0(1+\alpha\theta)^{\frac{2}{3}}$), and from the fact that ζ, which is Helmholtz's Gleitungs coefficient, has been proved by Meyer, Kundt, Warburg, and others to vary proportionally to the mean free path. It is usual to take

$$4\frac{\zeta_0}{R_0}$$

as a quantity negligible in comparison with 1. If this be permissible, then will

$$4\frac{\zeta_0}{R_0}\;\frac{\sqrt[6]{1+\alpha\theta''}}{1+\beta\theta''}$$

within the limits of the present interval of temperatures also be negligible. For the coefficient

$$\frac{\sqrt[6]{1+\alpha\theta''}}{1+\beta\theta''}$$

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[1] Nahrwold: Wied. Ann., vol. 31, 1887, p. 473; vol. 35, p. 120, 1888.

[2] Berliner: Wied. Ann., vol. 33, 1888, p. 289.

[3] Kayser: Wied. Ann., vol. 34, 1888, p. 607.

[4] Prof. Cleveland Abbe kindly called my attention to it.

[5] Nahrwold: Wied. Ann., vol. 35, 1888, p. 120.

[6] Elster u. Geitel: Wied. Ann., vol. 31, 1887, p. 109.

at 500°, 1,000°, 1,500°, is not greater than 1.15, 1.22, 1.23, respectively; whereas its probable maximum is reached at an earlier temperature. Hence, if the views maintained at the present stage of molecular kinetics be indeed correct, then no effect of the thermal variation of the coefficient of external friction need in the present work be apprehended. This is an important inference, for it might easily be supposed that the relation which Holman found to hold between 0° and 100°

$$\left(\frac{\eta''}{\eta_0}=1+0.002751\,t-0.00000034\,t^2\right)$$

might be progressively retarded in proportion as high temperatures are reached, by the gradually increasing values of

$$\left(1+4\frac{\zeta}{R}\right)$$

and in this way lead to the results which I have found.

Advantages of an exponential law.—It is next desirable to examine into the reasons in virtue of which, at the present stage of research, the equation $\eta=\eta_0\,(1+\alpha\theta'')^{\frac{2}{3}}$ may be accepted preferably to any other form. I will state here, inasmuch as one of the chief purposes of the present investigation is the introduction of a new instrument of high-temperature measurement, that any exponential form $(1+\alpha\theta'')^n$ which is in good accordance with the observations in hand is particularly acceptable, because it facilitates the calculation of thermal data by the principle of viscosity. Hence, when the choice is open between a number of equations, apparently of equal availability, the exponential form will always be adopted, because of the practical advantages just stated. Strictly speaking, the formula accepted for η'' $(\eta''=\eta_0(1+\alpha\theta'')^{\frac{2}{3}})$ is applicable to the case of a diatomic gas. In the case of monatomic gases, the supposition that the atoms are hard elastic solids leads to the law $\eta''=\sqrt{1+\alpha\theta''}$, as Maxwell and Meyer have elaborately shown.[1] From this law Maxwell[2] was led to depart, after having made a series of experiments in which viscosity appeared to vary directly as the absolute temperature of the gas. Maxwell thereupon deduced a law of repulsion between the molecules of a gas varying inversely as the fifth power of the distance between them, an acceptation by which his equations were capable of much simplification. Inasmuch as all the subsequent experiments made by many observers have failed to confirm Maxwell's experiments, it appears from this and from other evidence which Meyer[3] adduces that Maxwell's law of fifth powers is untenable. No other law of repulsion between molecules having

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[1] Maxwell: Phil. Mag. (4), vol. 19, 1860, p. 31; Meyer: Pogg. Ann., vol. 125, 1865, pp. 177, 401, 564.

[2] Maxwell: Phil. Trans., I, p. 249, 1866.

[3] Cf. Maxwell: Phil. Mag. (4), vol. 35, 1868, pp. 129, 185. Meyer: Kinetische Theorie der Gase, § 77.

since been proposed, the question regarding the thermal variations of viscosity which depends on the said law remains theoretically unsolved. Hence, between forms of an equation for η'' as a function of temperature, it is permissible to select the one among many applicable forms which confers the greatest practical advantage.

In the present instance (to give an example bearing on the remarks just made) there is another form of equation which, besides its inherent simplicity, might be applied to reproduce the observations in hand. This is $\eta''=\eta_0 (1+\gamma\theta'') (\sqrt{1+\alpha\theta''})$, which means that $L_t=L_0 (1+\gamma\theta'')$, and it seemed to me by no means idle to attempt to get some comparison with regard to the relevancy of these two forms. I think this can best be done by computing the zero value of $\frac{\eta''}{\eta_0}$ (which must be a unit of course) from the high-temperature values of $\frac{\eta''}{\eta_0}$, on the basis of each of the laws cited. Table 91, the data of which are taken from Tables 86 to 89, contains the results.

TABLE 91.—*Calculated zero values of* $\frac{\eta''}{\eta_0}$.

[$\alpha=0.00367$.]

	θ''	$\frac{\eta''}{\eta_0}$	$\frac{\eta''}{\eta_0}\frac{1}{(1+\alpha\theta'')^{2/3}}$	Error.	$\frac{\eta''}{\eta_0}\frac{1}{\sqrt{1+\alpha\theta''}}$	$\gamma\times10^6$
Air (Table 86) ..	° 565	2.068	0.98	+0.02	1.18	318
	592	2.100	0.97	+ 3	1.18	304
	995	2.678	0.96	+ 4	1.24	243
	1,216	3.123	1.01	− 1	1.34	277
Air (Table 89) ..	442	1.969	1.01	−0.01	1.22	489
	569	2.150	1.01	− 1	1.22	394
	982	2.713	0.98	+ 2	1.26	270
	1,210	3.219	1.04	− 4	1.38	315
H_2 (Table 87) ...	961	2.727	1.00	±0.00	1.28	295
	1,212	3.535	1.14	−0.14	1.52	425
H_2 (Table 88) ...	418	1.957	1.05	−0.05	1.23	550
	512	2.122	1.05	− 5	1.25	490
	520	2.138	1.05	− 5	1.25	489
	952	2.796	1.03	− 3	1.32	336

Turning first to the air points of Table 91, it appears clearly that the errors

$$1-\frac{\eta''}{\eta_0}\frac{1}{(1+\alpha\theta'')^{2/3}}$$

in the results referring to Tables 86 and 89 are promiscuous in distribution, and not larger than is quite compatible with the extreme difficulties of experiment. In the hydrogen points the same errors, though larger, are of a nature which can easily be interpreted. The large discrepancy at 1,212° in the results from Table 87 has been referred to permeability of platinum to hydrogen at this temperature. The errors in the results from Table 88 are nearly constant in value, showing clearly that the value of η_0, inserted into these computations, was too low. The nearly constant errors occurring here do not, therefore, in any degree invalidate the law $\eta''=\eta_0\,(1+\alpha\theta'')^{\frac{3}{4}}$, but furnish the best of evidence to corroborate it. Indeed, the plan here adopted of calculating the constant quantity $\left(\frac{\eta''}{\eta_0}\right)_0$ is singularly well adapted to exhibit the true character of the experiments made.

On the other hand, the right-hand division of Table 91 would show that the errors

$$1-\frac{\eta''}{\eta_0}\,\frac{1}{\sqrt{1+\alpha\theta}}\,\frac{1}{1+\gamma\theta''}$$

where $29<\gamma\times 10^5<37$ is to be introduced, are of a more serious kind than before. I have, therefore, contented myself in Table 91 with giving the individual values of γ.

Effect of imperfect gaseity.—The fact which most seriously antagonizes the relation

$$\eta''=\eta_0\,(1+\alpha\theta'')^{\frac{3}{4}}$$

is the occurrence in the case of air and for temperatures below 200°, of a mean exponent of $(1+\alpha\theta'')^n$, which is larger than $\frac{3}{4}$. O. E. Meyer's data for n lie between $\frac{2}{3}$ and $\frac{3}{4}$; Puluj's between 0.56 and 0.72; Warburg finds $n=0.77$, v. Obermayer $n=0.76$. Holman's elegant method leads to data which lie decidedly above 0.75, and which are of such a kind as to induce him to discard the exponential form of function altogether. Fully cognizant of the purposes Mr. Holman had in view in representing his results by a series of ascending powers of θ'', I nevertheless think that at the present stage of research a conservative policy is wiser. Results lying within an interval of only 200° above 0° C. can not be depended upon as furnishing a definite or final critique. Moreover, a formula which fails when tested by exterpolation has no further interest than the special one to which the author has applied it. The expansion of $\frac{\eta''}{\eta_0}$ in terms of a limited number of powers of θ'' alternately opposite in sign will lose all significance when applied beyond the interval of observation, and if the interval be small the use of such a formula scarcely justifies the labor involved in the computation. I have, therefore, preferred to retain the older formula

$$\eta''=\eta_0(1+\alpha\theta'')^n$$

and have endeavored to ascertain whether reasons might not be found in virtue of which n would tend to increase in proportion as low temperatures (0° C.) are approached. My experiments refer principally to temperatures above 400°, temperatures at which the conditions of perfect gaseity may be more justifiably accepted *a priori* and within which the true law of gases may be more clearly discerned. Dissociation is of course excluded from the nature of the gases chosen. Passing from high to low temperature, it appeared to me that E. Wiedemann's results are available for the interpretation of the discrepancy in question. For Wiedemann found that the exponent $n=0.73$ for air between 0° and 100° actually changed to $n=0.67$ for temperatures between 100° and 185°. But the latter value $n=0.67$ is practically indentical with the exponent $\frac{2}{3}$ which my experiments prove to hold as far as 1,330°. The conclusion, therefore, is natural that below 200° air does not rigorously fulfill the conditions of a perfect gas.

Looking for further data to substantiate this inference, it is well to remark that the frictional effect of decreasing temperature from the high to the low value is twofold in character; the purely kinetic friction is necessarily decreased. In proportion as temperature decreases, however, the gas manifests cohesive friction in increasing degree. In other words, at low temperatures the phenomenon of residual affinity becomes of sufficient importance to lead to the formation of molecules, the parts of which cohere more or less loosely for a greater or shorter period of time. The occurrence of ephemeral molecular aggregates[1] at low temperatures seriously complicates the interpretation of the observed phenomena, and equations for the kinetics of imperfect gases have been investigated only in a few instances. It is known, however, from the experiments of many observers, among whom v. Obermayer has examined the greatest number of correlative results, that both the exponents n of the above formula, as well as the coefficients of thermal expansion show a very marked tendency to increase in proportion as the gas loses the properties of a perfect gas and tends to become vapor. These known facts are almost conclusive evidence in favor of the view I have expressed, and the large exponent n which applies for air at low temperatures may be looked upon as a criterion of imperfect gaseity.

All these inferences are materially substantiated by the data obtained for hydrogen. Puluj's low temperature exponent for hydrogen is $n=0.69$; Warburg's $n=0.63$; v. Obermayer's $n=0.70$. Hydrogen, therefore, being (*cæt. par.*) more nearly a perfect gas than air, shows the same value of n at all temperatures above zero as far as I have observed; or, in other words, shows at zero the same law which in the case of air begins to apply at temperatures above 200°. Probably the strongest evidence in favor of the law I adduce is the fact that at high temperatures air and hydrogen behave identically, or that the same law

$$\eta''=\eta_0\,(1+\alpha\theta'')^{\frac{2}{3}}$$

appertains to each. This is proved conclusively by Tables 81 to 89, despite all thermal and incidental errors which the tables may contain. For these errors, affecting both gases alike, will not interfere with the identity of behavior, should it obtain. My data show that it does.

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[1] Cf. Natanson: Wied. Ann., vol 33, 1888, p. 683.

THE NEW METHOD OF PYROMETRY.

Methods of computation.—In view of these harmonious results, I am induced to place great reliance on the accuracy of the relation

$$\eta'' = \eta_0\,(1+\alpha\theta'')^{\frac{2}{3}},$$

as a law, which in the case of a diatomic perfect gas like air or hydrogen expresses the thermal variations succinctly. Subject to the validity of this law, the favorable character of my results therefore introduces a new method of high-temperature measurement; for by applying the Poiseuille-Meyer equation to transpiration data, such measurements can be made absolutely, throughout a wider thermal range, and with much greater convenience and accuracy than is the case with any other known method, not excepting the air thermometer. Moreover, the exclusive dependence of thermal data on the coefficient of thermal expansion can now be put to the test inasmuch as a series of analogous data may be investigated on the basis of the above relation, and the two series of data can be compared throughout the whole interval of temperature observed.

Introducing $\eta''=\eta_0\,(1+\alpha\theta'')^{\frac{2}{3}}$ into Meyer's equation, and solving with respect to θ'', the following form results:

$$\frac{(1+\alpha\,\theta'')^{\frac{5}{3}}}{(1+\beta\,\theta'')^{4}} = \frac{\pi}{16}\,\frac{1+4\,\frac{\zeta''}{R''}}{\eta_0}\,\frac{P^2-p^2}{76}\,\frac{t''}{V_0}\,\frac{R_0''^4}{l''}$$

$$-\frac{1+4\frac{\zeta''}{R''}}{1+4\,\frac{\zeta}{R}}\,\frac{R''^4_0}{R_0^4}\,\frac{l'+l'''}{l''}\,(1+(\alpha+\gamma)\theta) \quad . \quad . \quad . \qquad (11)$$

or more simply

$$\frac{(1+\alpha\,\theta'')^{\frac{5}{3}}}{(1+\beta\,\theta'')^{4}} = \frac{\pi}{16\,\eta_0}\,\frac{P^2-p^2}{76}\,\frac{t''}{V_0}\,\frac{R_0''^4}{l''} - \frac{R_0''^4}{R_0^4}\,\frac{l'+l'''}{l''}\,(1+\overline{\alpha+\gamma}\,\theta) \quad . \qquad (12)$$

Here η_0 is the zero-viscosity of the gas selected for temperature measurement. θ denotes the temperature of the cold ends of the capillary platinum tube, and γ is Mr. Holman's coefficient for air, approximately $\gamma=0.00275$. The remaining variables have the signification given on page 253. R_0'' and R_0 being respectively the radii of the hot part (l''), and cold parts (l', l''') of the capillary tube at 0° C., are practically equal in my apparatus. Hence, to reproduce the temperature, in Tables 86 to 89 from the measurements of viscosity made, the equation takes the simple form

$$\frac{(1+\alpha\,\theta'')^{\frac{5}{3}}}{(1+\beta'\,\theta')^{4}} = \frac{\pi\,R_0^4}{16.76.\;\eta_0\,l'}\,\frac{t''}{V_0}\left(P^2-p^2\right) - \frac{l'+l'''}{l''}\,(1+0.0064\;\theta) \quad . \qquad (13)$$

or

$$\frac{(1+\alpha\theta'')^{\frac{5}{3}}}{(1+\beta\theta'')^{4}} = A\,\frac{t''}{V_0}\left(P^2-p^2\right) - B\,(1+0.0064\;\theta) \quad . \quad . \qquad (14$$

a form which also includes equation (12), since A and B are constants. In the case of any instrument the capillary bore of which is variable along the length of the tube, or which can not be determined, A and B may be found by exposing the viscosity pyrometer to two known temperatures. For greater accuracy such an instrument may be directly compared with the air thermometer in the way soon to be indicated. In this place it is pertinent to call to mind certain valuable properties of the explicit equations (12) and (13). In the first place it is clear, inasmuch as the right-hand member of the equations varies as the $\frac{5}{3}$ power of absolute temperature, that the transpiration thermometer is unusually sensitive to variations of temperature. Again it appears that the one consideration in which the equations might seem to be of questionable applicancy, viz, the occurrence of the fourth power of $(1+\beta\theta'')$, becomes of less serious moment because this expression only effects $1+\alpha\ \theta''$ in the 2.4 power of $(1+\beta\theta'')$. Hence the coefficient of thermal expansion of platinum, it known with an accuracy of only 10 per cent., would not affect the result more than 0.2 per cent. at 1,000°. Furthermore, in the case of known fixed thermal data, like those discussed in Chapter II, β may be *directly* determined from transpiration measurements made with the instrument itself. For it is merely necessary to solve equation (14) with respect to β in order to determine this constant with the same degree of accuracy with which it is to be used. Finally the quantity

$$\frac{R_0^4}{\eta_0}$$

which enters into equations (12) and (13) can also be directly determined from measurements made at the low temperature. For, disregarding the unessential correction members, equation (5), on page 253 shows at once that

$$1 : \frac{R_0^4}{\eta} = \frac{\pi}{16.76.\ L}\frac{t''}{V_0}(P^2-p^2)$$

in which if the measurements are made at θ, η may be reduced to η_0 by Holman's coefficient. With this operation the fiducial zero of the viscosity apparatus may be said to be determined. R_0^4/η_0 is more accurately determinable in this way than by gravimetric measurement of R.

Results.—To give emphasis to the remarks on the probable excellence of the viscosity pyrometer, I will use the data in Tables 86 to 89 for the calculation of temperatures from data based on the viscosity of the gases operated with. In Table 92, θ'' denotes the temperature, thermo-electrically measured, at the points of the helix shown in the diagram, Fig. 47*a*. $[\theta'']$ is the corresponding datum of the transpiration pyrometer.

TABLE 92.—*Temperatures measured thermo-electrically and by the transpiration pyrometer.*

	θ''	$[\theta'']$	Diff.		θ''	$[\theta'']$	Diff.
Air	520	511	+ 9	Hydrogen.	958	956	+ 2
	562	549	+13		960	958	+ 2
	567	558	+ 9		962	959	+ 3
	586	572	+14		962	960	+ 2
	598	583	+15		970	975	− 5
Air	994	964	+30	Hydrogen.	1209	1329	−120*
	994	963	+31		1212	1338	−126
	996	966	+30		1215	1337	−122
Air	1212	1217	− 5	Hydrogen.	414	434	− 20
	1217	1227	−10		416	437	− 21
	1219	1222	− 3		421	441	− 20
					423	445	− 22
Air	430	442	−12				
	436	450	−14	Hydrogen.	507	529	− 22
	446	458	−14		513	535	+ 22
	455	467	−12		515	536	− 21
					518	541	− 23
Air	563	571	− 8		520	543	− 23
	568	574	− 6		521	543	− 22
	570	577	− 7				
	575	580	− 5	Hydrogen.	946	963	− 17
					952	968	− 16
Air	975	965	+10		954	974	− 20
	981	971	+10		955	976	− 21
	990	981	+ 9				
Air	1209	1245	−36				
	1210	1245	−35				
	1210	1247	−37				

* Platinum pervious to hydrogen.

The errors of this table are apparently large in places; but they are by no means excessive when the great difficulties of experiment are justly taken into account. The observation of especial importance here is that the distribution of errors is promiscuous. A difference of 125° occurs in the case of hydrogen transpiring at 1,200°; but at this temperature platinum is seriously pervious to hydrogen. In some measure the errors are due to the fact that the gases referred to the same η_0 were not absolutely identical in composition. This is particularly the case in the final data for hydrogen in which the nearly constant error −20° is due to the erroneously low η_0 here inserted—as I have already pointed out, page 271. Beyond this I believe that the differences of temperature remaining indicate actual differences of thermal environment for the two thermometers here compared. They show that throughout the space enveloping the two pyrometers temperature was not rigorously constant, and it is quite in keeping with the present method of experiment to suppose that the mean temperature, θ'', of three points as given by the thermo-element, and the mean temperature $[\theta'']$, for the length of nearly 67^{cm} of platinum capillary tube, will not even in the final experiment have been identical within 20° at 1,000°. Taking the transpiration data alone they manifest a striking degree of accordance even above 1,300°, as may be readily proved by the earlier tables, 81 to 85. Again the uniformity of variation of a given thermal datum, whether measured thermo-electrically or by the transpiration pyrometer, proves beyond a doubt that high thermal data are measurable at 1,000° in terms of the viscosity in gases with an accuracy of a few tenths of a degree.

TRANSPIRATION NOT SUBJECT TO THE POISEUILLE-MEYER LAW.

Objects of the investigation.—The chief difficulty in operating with capillary tubes of a bore so fine that Meyer's formula is rigorously applicable at low temperatures as well as at high temperatures lies in the fact that the flow in such tubes almost ceases when the degrees of white heat are approached. There are a number of ways of obviating this annoyance, in the first of which fascicles of tubes are used side by side; in the second of which the transpiring volumes are measured in graded apparatus, so that at high temperatures small volumes may be measured as accurately as large volumes at low temperatures. Again, transpiration may be allowed to take place through graded capillary tubes of platinum the length or bore of which increases by some given law; or with the slow current in continuous flow, rates of transpiration $\left(\frac{V_0}{t}\right)$ may be measured by some applicable method of repetition.

It is nevertheless desirable, however well these means suffice for the attainment of the end in question, to try to arrive at practical results relative to tubes of a bore so large that Meyer's formula is no longer applicable. All these endeavors are decidedly in the interest of expeditious work, for I find that compared with each other such measurements are not lacking in accuracy, although the total time consumed for observation may not exceed a minute.

To make these observations greater volumes of air are necessary. Hence I have found it desirable to measure the volumes before they enter the platinum capillary tube. I mention this here to point out an important peculiarity of the above apparatus. It is easily possible so to adjust it that the gas may be measured both *before entering* and *after leaving* the platinum capillary. The observer then has it in his power not only to detect the presence of gross leaks in the apparatus with certainty, but to follow the gas in its motions either (normally) through the capillary canal or (by diffusion) through the white-hot walls of platinum tube.[1] Moreover, it will be noted that the experiment in gaseous flow through capillary tubes are accompanied by something remotely similar to self-induction on opening and on closing the circuit. For when the stop-cock K in Fig. 45 is opened, the air rushes in the dead space

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[1] See remarks relative to impure hydrogen, p. 275.

between stop-cock and capillary tube until the high pressure P is reached; and after closing the stop-cock the compressed air of the dead space is gradually discharged. The method of eliminating the positive error which is thus added to the transpiration volume (V_0) has been indicated on page 257. But when the transpiration volume has to be chosen small the dead space discrepancy is more serious in character even when reduced to the smallest value compatible with the practical efficiency of the apparatus. These difficulties are quite avoided by using tubes of large bore and larger volumes of gas, and hence a second reason why the experiments of the present paragraph are desirable.

Hoffmann's researches.—From a theoretical point of view[1] the considerations involved are, of course, of extreme difficulty and complicated in mathematical character. As such they must be here omitted. From an experimental point of view, the difficulties encountered are fortunately less formidable, and an excellent analysis of the subject, based on a variety of observations, has been published by Hoffmann.[2]

Hoffmann, after recognizing that the chief discrepancy is introduced at the ends of the tubes, derives his first equation by successively applying Navier's equation $vp=R^2\,\pi\,\pi_1\sqrt{C\ln\frac{p_1}{\pi_1}}$ for the ends of his tubes, and the Poiseuille-Meyer equation for the intermediate parts. Unfortunately, even in the favorable case of slight variation from Poiseuille-Meyer's law, this process leads to very involved results:

$$vp=\frac{R^4\,\pi\delta g\,(\pi_1^2-\pi_2^2)}{16\,\eta l}$$

$$\pi_1=\frac{p_1\left\{1-\frac{2\,(vp)^2}{R^4\,\pi^2\,Cp_1^2},\right.}{e^{\frac{(vp)^2}{R^4\pi^2\,Cp_1^2}}-\frac{2\,(vp)^2}{R^4\,\pi^2\,Cp_1^2}}$$

$$\pi_2=p_2\,e^{\frac{(vp)^2}{R^4\pi^2\,Cp_2^2}},$$

where p_1 and p_2 are the observed pressures just before entering and leaving the capillary tube, and π_1 and π_2 are the corresponding pressures in the first and final section; $C=\frac{2\delta g\,.76\,(1+\alpha\vartheta)}{0.00129277}$ and the remaining variables have a meaning which is easily understood from the discussion on page 253. $\pi=3.1416$ and e is the basis of the Naperian

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[1] The literature is digested by Hoffmann (l. c.) as follows: Navier: Mém. de l'Acad. de sc. de Paris, vol. 6, 1823, p. 389; Poisson: Journale de l'école Polytechnique, vol. 13, 1831, p. 139; Stokes: Trans. Cambridge Philos. Soc., vol. 8, 1849, p. 287; Cauchy: Exerc. de Mathém., vol. 3, 1828, p. 183; de St. Venant: C. R., vol. 17, 1843, p. 1240; Stefan: Wien. Ber., vol. 46 (2), 1862, p. 8.

[2] Hoffmann: Wiedemann, Annalen Physik, new series, vol. 21, 1884, p. 470,

logarithms. Unfortunately these values of π_1 and π_2 themselves contain vp, for which, however, the approximate value given by Poiseuille-Meyer's law may usually be substituted with sufficient accuracy.

In view of these difficulties Hoffmann investigates an empirical relation by observing that (cæteris paribus) the certain small length of maximum efflux is subject to Navier's law, whereas as length increases the efflux obeys Poiseuille-Meyer's law. If, therefore, time of efflux (cæteris paribus) be studied as a function of length, Navier's law fixes a point, while Poiseuille-Meyer's law fixes an oblique line passing through the origin. Hoffmann then supposes on the basis of his experimental results that the actual passage from the point to the line takes place nearly along an hyperbola, of which the said point is the vertex and the said line the asymptote. A suitable modification of this hypothesis leads Hoffmann to the equation

$$vp=\frac{1}{\sqrt{\frac{1}{P_1^2}+\frac{1}{(N_1ab)^2}}}$$

where

$$P_1=\frac{R^4\pi\delta g\,(p_1^2-p_2^2)}{16\eta\, l}$$

$$N_1=\frac{R^2\pi\,(p_1+p_2)}{2}\sqrt{\frac{C}{0.43429}\log\frac{2p_1}{p_1+p_2}}$$

and where $b=(l+4)\,(2\,l+4)$ and a has a tabulated value of nearly 1, but varying with the mean difference of pressure.

Hoffmann's equation contains difficulties of calculation of a very tedious and impracticable kind, particularly in view of the involved occurrence of the factor C, which represents the thermal variations of the transpiring gas. With full deference, therefore, for the accuracy of application which Hoffmann has reached in his results, I shall nevertheless compute η by the formula (5) on page 253, above; i. e., directly by the Poiseuille-Meyer law. Having done this, it was my further object to find from the known law of variation of η with temperature, what correction was to be applied to the Poiseuille-Meyer equation, to make the data for tubes not rigorously capillary conform with the data already in hand for truly capillary tubes. The plan which I have in mind is somewhat different from that of Hoffmann and more in harmony with the general tenor of my experiments. The form which I aim to give my correction is an exponential, in which the dimension of the capillary tube and the actual viscosity of the transpiring gas are the variables. I found, however, that to do this satisfactorily it would be necessary to repeat my experiments at greater length than I am now justified in doing; and observing that the data which I have in hand make up a diagram of the transpiration phenomenon in wide tubes, of remarkable clearness and full of suggestion, I resolved to communicate these without elaborate reductions.

EXERIMENTAL RESULTS.

Transpiration under variable pressure P—p.—I shall introduce these results by a number of experiments made at the outset of the present investigation, inasmuch as these have a direct bearing on the feasibility of the transpiration apparatus for pyrometric purposes. In these experiments neither Mariotte flask nor lateral tube was employed, so that the pressure fell from the initial to the final value at one end of the tube, the other being at atmospheric pressure. The helix itself was wound in a flat form of large radius so as to lie completely in the zone of fusion of the Bunsen burner. For each special part of the table the conditions of flow, however complex, are the same. t is the time of efflux of the volume V; L and l denote the length of tube and cold ends; R is the internal radius. In Table 95 the tempestuous influx of mercury into the receiver B was avoided by opening the stop-cock of the Mariotte flask until the flow of mercury had ceased, and then opening the stop-cock of the capillary.

TABLE 93.—*Transpiration of air under variable pressure.* (*Burner not chimneyed.*)

[Capillary tube No. 1. $L=37^{cm}$. $l=8^{cm}$. $R=0.025^{cm}$. $V_0=580^{cc}$. $\theta=20°$.]

Time.	Initial pressure.	Final pressure.	Barometer.	Temperature.
98	108	97	78	20°.
459				Bright red heat (1,000°).
99				20°.
459				Bright red heat.
98				20°.
78	118	107	78	20°.
323				Bright red heat.
78				20°.
314				Bright red heat.
78				20°.
189	143	132	78	Bright red heat.
57				20°.
187				Bright red heat.
55				20°.
187				Bright red heat.

TABLE 94.—*Transpiration of air under variable pressure. (Chimneyed burner.)*

[Platinum capillary tube No. 1. $L=87^{cm}$. $l=4^{cm}$. $R=0.0272^{cm}$. $V_0=580^{cc}$.]

Time.	Initial pressure.	Final pressure.	Barometer.	Temperature.
79	118	112	78	18°.
249				Bright red heat.
79				18°.
252				Bright red heat.
145	99	91	78	18°.
590				Bright red heat.
145				18°.
597				Bright red heat.

TABLE 95.—*Transpiration of air under variable pressure.*

[$L=37^{cm}$. $l=4^{cm}$. $R=0.0272^{cm}$. $\theta=5°$. $V_0=580^{cc}$.]

Time.	Initial pressure.	Final pressure.	Barometer.	Temperature.
73	120	114	77	15°.
244				Bright red heat.
74				15°
242				Bright red heat.
74				15°.
92	111	104	77	15°.
313				Bright red heat.
92				15°.
319				Bright red heat.
92				16°.
125	101	94	77	16°.
487				Bright red heat.
125				16°.
478				Bright red heat.
125				16°.
195	92	84	77	16°.
900				Bright red heat.
900				Bright red heat.
196				16°.

Transpiration under constant pressure P—p.—The following tables, 96 to 100, contain the results of precise experiments. As before, P and p are the pressures at the two ends of the platinum capillary, respectively; θ'' the temperature of its hot parts $L-(l'+l''')$, and θ the temperature of its cold parts. V is the zero-volume of air transpiring through the capillaries in the time t''. R is the radius of the capillary and τ the actual temperature of the air in the receiver B (Fig. 43), from which temperature τ the reduction to zero was made. $F(\theta'')$ has the above signification.

$$F(\theta'')=\frac{\eta''}{1+\frac{\zeta''}{4R''}}\div\frac{\eta_0}{1+\frac{\zeta_0}{4R_0}}$$

Unfortunately, the measurement of θ'' in all these experiments was made as shown in the diagram, Fig. 47, and hence these values are not so good as those in Tables 86 to 89 above (helix very compact). τ is directly read off on the thermometer T in the receiver B, in Fig. 44, and the correction may be applied either to t'' or to the final η''.

To measure V, I filled the receiver with mercury and weighed the volume of liquid contained. Similarly R was computed from the weight of the mercury thread which fills the capillary tube. But this operation in case of an opaque tube is very unsatisfactory. My plan was to seal the capillary helix (previously dried and weighed with care) into a glass tube with mastic, and then allow a current of mercury to pass through both. When all air was expelled I stopped up one end of the capillary with soft wax, then removed the glass tube, cleansed the helix, and weighed again. The weights so obtained differ enough to make errors of 5 per cent. and 10 per cent. in R^4 possible. Hence I put no stress on the absolute data, but consider them in their relative bearing only. For each such relative series R is constant. Perhaps volumetric methods might have led to better results (v. page 213), but I did not apply them.

To calculate η'' the formula on page 253 was employed in the usual way. This presupposes a knowledge of η for the cold ends, corresponding to each pressure observed. It is necessary, therefore, first to construct η as a function of pressure graphically, in order that the proper value may be inserted into the correction member of the formula for η''.

The error due to cold ends here in question bears an intimate relation to the Navier effect; and this method of correcting for it presupposes that both the cold part and the hot part of the capillary has *two* ends. Hence it would seem that as there are in all but *two* ends, instead of four, to the capillary tube experimented upon, that the correction applied is not valid. I think, however, the following results show that the departure from Poiseuille-Meyer's law observed with metallic capillary tubes is largely due to unavoidable roughness of the internal surface (*i. e.*, of the walls of the capillary canal), and hence the correction is warranted.

TABLE 96.—*Apparent viscosity of air at high temperatures. Absolute measurement.*

[Capillary tube No. 10. $L=33.43^{cm}$. $l'+l'''=2.7^{cm}$. $V=565.7^{cc}$. $R=0.00794^{cm}$. $\theta=7°$.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	$\frac{\eta}{1+4\zeta/R}$	θ'' °	$\frac{\eta''}{1+4\zeta''/R''}$	τ	$F(\theta'')$
*133.11	56.35	1506	232000	0.000272	0	0.000266	19.6	....
92.32	15.56	6545	224300	262	0	257	19.4	....
†124.69	48.04	1677	211600	0.000251	0	246	21.5	....
88.60	11.95	7930	204400	243	0	238	22.0	....
‡125.64	49.18	1683	218800	....	14	0.0002588	20.8	....
125.68	49.22	1660	216000	0.000256	0	‡2508	20.7	....
§125.22	48.86	18000	2321000	0.000255	977	6858	22.8	2.743
124.68	48.32	1678	213500	0.000254	0	2491	22.3	....

* First ajustment, $p=76.76$.
† Second adjustment, $p=76.65$.
‡ Third adjustment, $p=76.46$.
§ $p=76.36$.

TABLE 97.—*Apparent viscosity of air at high temperature. Absolute measurement.*

[Capillary tube No. 9. $L=$——. $R=0.0184^{cm}$. $V=566^{cc}$. $\theta=4°$. $l'+l'''=1.5^{cm}$. Thermo-couple No. 37.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ'' °	$\frac{\eta''}{1+\zeta''/R''}$	τ
*121.26	45.34	183	21550	4	0.000367	20.5
121.25	45.33	183	21550	4	365	19.2
121.24	45.32	183	21550	4	364	18.8
114.31	38.39	211	20290	4	343	18.5
114.16	38.24	211	20200	4	341	18.5
107.60	31.68	250	19150	4	324	18.5
107.54	31.62	250	19110	4	323	18.5
101.12	25.20	306	17980	4	302	18.3
101.10	25.18	306	17960	4	302	18.3
94.24	18.32	407	16710	4	282	18.0
94.23	18.31	405	16620	4	280	18.0
87.41	11.49	621	15350	4	259	17.8
87.44	11.52	616	15270	4	258	17.8
87.44	11.52	614	15220	4	257	17.8
†87.91	11.81	856	21790	100	0.000280	19.6
87.85	11.75	846	21420	100	275	19.9
94.81	18.71	556	23370	100	300	20.2
95.00	18.90	551	23420	100	301	20.1
101.45	25.35	419	24780	100	319	20.0
101.75	25.65	418	25060	100	322	20.1
115.51	39.41	283	28070	100	361	20.3
115.52	39.42	281	27890	100	359	20.3
123.44	47.34	241	29920	100	385	20.3
123.50	47.40	241	29960	100	385	20.3
‡124.10	47.89	1193	150100	1026	0.000591	21.0
124.24	48.03	1188	150100	1030	589	21.2
§88.33	12.25	5632	149200	1024	591	22.0
88.19	12.11	5624	147000	1021	586	23.0
‖124.16	48.20	1175	149200	1026	590	22.7
123.99	48.03	1187	150100	1026	592	21.5

* $p=75.92$. † $p=76.10$. ‡ $p=76.21$. § $p=76.08$. ‖ $p=75.96$.

TABLE 98.—*Apparent viscosity of air at high temperatures. Absolute measurement.*

[Capillary tube No. 3. $L=42^{cm}$. $l=4^{cm}$. $R=0.025^{cm}$. $V=566^{cc}$. $\theta=5^\circ$. Thermo-couple No. 37.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	$\frac{\eta''}{1+4\,\zeta''/R''}$	τ
*87.6	11.8	212	5120	° 5	0.000279	18.0
91.9	15.6	160	5480	5	299	18.0
97.0	20.7	127	5950	5	325	18.2
102.2	25.9	106	6410	5	351	18.5
107.6	31.3	91	6850	5	375	18.2
112.0	35.7	81	7120	5	389	18.2
117.1	40.8	73	7540	5	410	17.5
†88.3	11.3	220	5300	14	0.000285	....
93.2	16.2	162	5800	14	309	....
98.2	21.2	128	6156	14	328	....
103.2	26.2	106	6498	14	346	....
108.3	31.3	92	6930	14	369	....
113.5	36.5	81	7315	14	389	....
‡89.6	12.8	269	7460	100	0.000312	16.5
94.7	17.9	201	8030	100	336	16.5
100.5	23.7	156	8530	100	357	16.5
§92.0	15.0	1209	39800	941	0.000562	....
98.9	21.9	796	39740	941	560	....
105.7	28.7	585	39840	934	564	....
112.7	35.7	453	39840	933	564	....

* $p=76.8$. † $p=77.0$. ‡ $p=76.8$. § $p=77.0$.

TABLE 99.—*Apparent viscosity of air at high temperatures. Absolute measurement.*

[Capillary tube No. 4. $l'+l''=4^{cm}$. $L=42.5^{cm}$. $V=566^{cm}$. $R=0.025^{cm}$. $\theta=4^\circ$. Thermo-couple No. 37.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	$\frac{\eta''}{1+4\,\zeta''/R''}$	
*86.4	9.5	268	5390	° 4	0.000266	22
86.4	9.5	267	5400	4	267	22
89.7	12.8	204	5690	4	281	22
90.2	13.3	200	5780	4	285	21
90.8	13.9	194	5870	4	289	21
91.2	14.3	189	5920	4	292	21
96.5	19.6	146	6480	4	319	21
96.6	19.7	147	6530	4	321	21
101.6	24.7	121	6980	4	345	21
101.8	24.9	121	7010	4	345	21
106.9	30.0	104	7450	4	0.000368	22
107.0	30.1	103	7420	4	366	22
111.3	34.4	92	7750	4	385	21
112.2	35.3	90	7830	4	386	21
112.3	35.4	90	7840	4	382	21
115.1	38.2	85	8100	4	403	22
117.3	40.4	80	8170	4	400	22
†88.9	12.0	1000	25850	636	0.000428	19
89.0	12.1	1023	26850	658	435	19
123.7	46.8	260	31780	652	514	19
123.6	46.7	263	32060	658	516	19
95.8	18.9	665	28360	684	446	19

TABLE 99.—*Apparent viscosity of air at high temperatures. Absolute measurement*—Cont'd.

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	$\frac{\eta''}{1+4\zeta''/R''}$	τ
95.6	18.7	681	28670	° 695	447	20
116.7	39.8	317	31810	687	497	20
116.7	39.8	317	31810	690	496	20
106.1	29.2	431	29910	687	468	21
106.2	29.3	434	30330	689	474	21
123.7	46.8	268	32760	688	511	21
123.7	46.8	268	32760	687	511	21
‡95.2	18.9	697	29690	721	0.000451	20
95.2	18.9	724	30840	744	457	20
95.3	19.0	767	32910	786	471	19
123.4	47.1	305	37640	808	526	19
123.4	47.1	311	38390	848	518	19
95.2	18.9	835	35550	855	480	19
95.4	19.1	847	36510	860	491	19
123.2	46.9	327	40140	862	536	19
123.5	47.2	326	40340	864	537	19
95.4	19.1	864	37270	875	494	19
§123.5	47.3	363	44840	988	0.000545	22
123.6	47.4	366	45540	994	548	23
88.2	12.0	1721	44440	998	537	23
88.4	12.2	1688	44320	1004	535	23
123.6	47.4	366	45500	1005	545	24
123.5	47.3	369	45770	1005	549	24
88.3	12.1	1688	44220	1004	532	24

* $p=76.9$. † $p=76.9$. ‡ $p=76.3$. § $p=76.2$.

TABLE 100.—*Apparent viscosity of air at high temperatures. Absolute measurement.*

[Capillary tube No. 5. $L=35.1$. $R=0.025^{cm}$. $V=565.7^{cc}$. $\theta=7°$. $l'+l''=3.0^{cm}$.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	$\frac{\eta''}{1+\zeta''/R''}$	τ
*123.83	46.79	436	53200	1285	0.000585	19.4
124.76	47.72	426	53250	1286	585	19.6
124.53	47.49	428	53100	1286	584	19.8
89.20	12.16	1942	50840	1286	565	21.0
89.17	12.13	1935	50640	1297	567	22.0
†124.61	47.61	423	52700	1300	579	22.1
124.67	47.67	422	52660	1305	578	22.4
‡124.24	47.31	337	41690	1048	0.000541	22.8
124.07	47.14	338	41630	1045	541	22.5
88.90	11.97	1469	37910	1044	495	22.5
88.99	12.06	1458	37920	1043	495	21.8
124.31	47.38	334	41390	1035	540	22.0
124.11	47.18	334	41170	1035	538	22.0
§108.44	31.59	92	7008	7°	0.000386	22.0
109.07	32.22	90	7015	....	386	22.0
85.81	8.96	261	4949	....	273	22.5
85.63	8.78	263	4881	....	269	22.5
85.78	8.93	262	4951	....	273	22.5
108.96	32.11	90	6985	....	385	22.5
108.47	31.62	92	7015	....	386	22.5

* $p=77.04$. † $p=77.00$. ‡ $p=76.93$. § $p=76.85$.

Among these tables the first is unique, and I shall therefore specially refer to it. The capillary tube used is the same with which the data in Tables 81 to 90 were investigated; but for the large volume V_0 the time of efflux at red heat (977°) is five hours. During the whole of this time θ'' and P were measured so as to obtain a fair mean result and eliminate unavoidable fluctuations of temperature. It is exceedingly gratifying to observe that the value of $F(\theta'')$ computed from these observations conforms very well with the data of Tables 81 to 89, and with the law $\eta''=\eta_0(1+\alpha\theta'')^{\frac{2}{3}}$, despite the great difference of method of measurement employed. Differences of η_0 in different parts of the table are due to imperfections in the earlier adjustment; but the values of η_0 measured before and after the high temperature measurement agree satisfactorily. Variations of η_0 with P will be discussed below. The negative error of $F(\theta'')$ may also be anticipated, since in so long a period of efflux (five hours) even minute leaks in the compressing apparatus would produce appreciable results.

Transpirations compared differentially.—Before proceeding with the discussion of these results it is expedient to communicate the data obtained with a differential apparatus. The formula for this method of experimentation has already been given. Hence the results of the following Tables 101 to 103 need but little further elucidation. The adjustments here are identical in plan with those of the differential galvanometer. In Fig. 55, p. 305, air is supposed to enter at a and to pass through the stop-cock K, where the bifurcation of current is brought about. Supposing K open, a part of the air passes through the hot spiral H and thence to the measuring-tube V_g; the remainder through the cold helix C, and thence to the measuring-tube V_h. V_h and V_g corresponding respectively to the temperature θ and θ'' are given in the Tables. If $\theta=\theta''$, then the results contain data for the computation of the ratio of the radii of the two helices. If $\theta''>\theta$, the results lead to

$$F_1(\theta'')=\frac{\eta''}{1+\frac{4\zeta''}{R''}} \bigg/ \frac{\eta}{1+\frac{4\eta}{R}}$$

the beauty of the method being this, that time and pressure measurements (in the case of capillary tubes of very small bore) are superfluous. I have purposely used tubes of large bore however. From $F_1(\theta'')$,

$$\eta'' \bigg/ \left(1+\frac{\zeta''}{4R''}\right)$$

may be calculated by inserting the corresponding values of η from Tables 96 to 100.

TABLE 101.—*Differential measurement. Apparent viscosity of air at high temperatures.*

[Capillary tubes Nos. 5 and 6. $l'+l''=0$. $l'=35.1^{cm}$. $L=35.1^{cm}$. $R=0.025^{cm}$. Couple No. 37. $p=75.3$. $\theta=4^{\circ}$.]

$P-p$	V_h	V_g	$\frac{\eta''(1+\frac{4\zeta''}{R_1})}{\eta(1+4\zeta/R_2)}$	θ''	P	R_h/R_g
				°		
16.7	48.51	52.17	....	4	92.1	0.928
15.1	46.01	50.42	....	4	90.4	0.911
11.5	48.09	52.57	....	4	86.9	0.914
8.9	48.44	51.22	....	4	84.3	0.946
....	47.14	48.06	....	4	....	0.981

$P-p$	V_h	V_g		θ''	P	
7.9	51.3	16.5	1.30	454	88.4	....
11.0	50.2	16.5	1.22	483	86.5	....
16.2	50.7	16.9	1.15	505	91.7	....
20.6	52.0	16.5	1.18	531	96.1	....
25.8	48.4	18.6	0.92	578	101.3	....
31.1	48.6	16.7	0.99	617	106.6	....
27.8	46.2	16.4	0.96	620	103.3	....
23.1	45.7	15.4	1.02	612	98.6	....
19.2	50.2	16.9	1.03	604	94.7	....
14.0	50.3	16.0	1.10	594	89.5	....
9.2	50.8	14.6	1.22	589	84.7	....

TABLE 102.—*Differential measurement. Apparent viscosity of air at high temperatures.*

[Capillary tubes Nos. 5 and 6. $l'+l''=5^{cm}$. $l''=30.0^{cm}$. $L=35.0^{cm}$. $R=0.025^{cm}$. $p=76.2$. $\theta=946^{\circ}$].

$P-p$	V_h	V_g	$\frac{\eta''(1+\alpha\theta'')}{\eta(1+\alpha\theta)}\frac{(1+\beta\theta)^4}{(1+\beta\theta'')^4}$	θ''	P
48.3	50.54	42.06	1.87	(1200)	124.5
12.0	51.95	39.87	1.48	....	88.2
48.2	52.59	44.19	1.36	....	124.4
11.9	51.59	40.26	1.46	....	88.1
11.8	51.09	34.86	1.66	(1300)	88.0
49.3	51.62	37.46	1.57	....	125.5
11.8	49.79	35.76	1.58	....	88.0
51.7	52.77	41.36	1.45	1160	127.9
12.4	52.69	38.51	1.56	1160	88.6
51.7	50.99	38.31	1.51	1160	127.9
51.6	52.19	36.29	1.63	1280	127.8
12.3	51.87	34.29	1.71	1280	88.5
53.0	52.02	37.61	1.57	1280	129.2

TABLE 103.—*Differential measurement. Apparent viscosity of air at high temperatures.*

[Capillary tubes Nos. 5 and 6. $l'+l'''=4^{cm}$. $l''=30.4^{cm}$. $L=41.2^{cm}$. $R=0.0184^{cm}$. Thermo-couple No. 37. $\theta=4^{\circ}$.]

$P-p$	V_h	V_s		θ''	P	p	R_h/R_s	
39.9	43.8	52.5	....	4	117.4	77.5	1.00	....
10.7	44.7	52.2	....	4	88.2	77.5	1.03	....
10.7	43.3	51.9	....	4	88.2	77.5	1.00	....
10.8	43.6	52.1	....	4	88.3	77.5	1.00	....
39.8	44.4	51.3	....	4	117.3	77.5	1.04	....

$P-p$	V_h	V_s	$F(\theta'')$	θ''	P	p	$\frac{\eta}{1+\frac{4\zeta}{R}}$	$\frac{\eta''}{1+\frac{4\zeta''}{R''}}$
44.0	51.2	16.2	1.88	587	121.5	77.5	0.000362	0.000501
11.9	51.9	12.2	1.78	605	89.4	77.5	259	461
44.6	51.0	15.4	1.37	614	122.1	77.5	364	498
11.7	52.1	11.5	1.86	624	89.2	77.5	258	480
44.5	51.8	14.9	1.40	630	122.0	77.5	363	508
44.7	51.6	9.54	1.61	973	122.3	77.6	0.000364	0.000587
11.7	52.5	7.22	2.17	974	89.3	77.6	258	560
44.8	52.1	9.51	1.63	977	122.4	77.6	364	593
11.4	52.8	7.05	2.23	977	89.0	77.6	257	574
45.2	51.5	9.40	1.63	978	122.8	77.6	365	596
11.5	52.4	6.96	2.24	979	89.1	77.6	258	578

It was not my object in this place to carry this method to a high degree of perfection, but rather to show the feasibility of measurements made in this expeditious and simple way. This the tables effectually do. Table 101 shows that for tubes of the large radius $R=0.025^{cm}$ the results are not accurate when so small a volume as $V=50^{cc}$ transpiring at zero, is made the standard of comparison. They are irregular. On the other hand, when the standard volume transpires at high temperatures ($\theta=900^{\circ}$ and $\theta''>\theta$), this method proves to be quite feasible and the results regular (Table 102). For tubes of finer bore ($R=0.018^{cm}$), Table 103 shows that the data are consistent at all temperatures.

Fortunately, in the differential method the errors due to the dead space between stop-cock and the capillary, if this space be made small, is nearly eliminated.

DISCUSSION.

Apparent viscosity and pressure.—To obtain a clear insight into the data of these tables, it will be necessary to construct them graphically. This has been done in Fig. 54, p. 304, in which the abscissæ are $P-p$, and the ordinates the value of η'' given by the Poiseuille-Meyer formula, by inserting in it the given constants of the apparatus and the value of the pressure, time, and volume data observed. Commencing with Table

96, which contains data for the smallest radius occurring in the present work, $R=0.0079^{cm}$, it appears that the value of η_0 increases very perceptibly as $P-p$ increases. The different lines drawn correspond to differences in bore of the readjusted tubes. At 9.80°, owing to the length of time of a single observation, only one datum is at hand. Turning thence to Table 97, which holds for tubes of a larger bore ($R=0.0184^{cm}$), the values η_4 η_{100} . . . are found to lie on very nearly straight lines, which, in comparison with those of the preceding table, have increased enormously in obliqueness; η therefore increases at a rapid rate with $P-p$, which rate, however, diminishes as temperature increases, and is nearly zero at 1025°. Now, inasmuch as the rate of axial transpiration decreases with temperature, and inasmuch as Meyer's formula fails for values of the velocity of the particles above a certain datum, these curves suggest that the observed decrement of slope of the lines produced by temperature is due to the decrease of the axial velocity of the transpiring particles produced by the same cause. In this place the differential results of Table 103 are available, and furnish data for η_{625}. The values for η_{975}, which Table 103 also contains, are, in general, in good accordance with the data of Table 97, and are therefore not essential to the diagram.

Tables 98, 99, and 100 contain results for the largest value of radius, $R=0.027^{cm}$, occurring in these experiments. In Table 98 the results η_5, η_{14}, η_{100}, show a tendency to curvilinear loci. But the true character of the phenomenon appears none the less clearly. The mean rate of increase of η with $P-p$ is distinctly larger than in the previous instance (Table 97). Again the slope decreases as temperature increases, and is practically zero at 930°. Here, therefore, the effect of the axial velocity of the transpiring particles is again apparent.

Table 99 is more full as regards the sequence of data contained, as well as more accurate; η_4 shows a tendency to curvature, but the points may serviceably be grouped on a straight line; η_{676} is the mean of the first set of results for temperatures of the Argand air-bath. Inasmuch as pressures are high and low alternately in both this series and the next, the line connecting corresponding observations has fair claims to accuracy. The data substantiate the inferences drawn with reference to Table 88. The lines are all oblique and they approach horizontality in proportion as higher temperatures are reached.

I may notice here that in case of high temperatures the cooling effect of air passing through the capillary under high pressure was very distinctly discernible, the thermo-couple showing differences of 20° to 40° between the maximum and minimum rates of flow.

Table 100 finally contains results of my largest radius, $R>0.027^{cm}$, the exact value of which I do not now care to measure, because the capillary apparatus has been carefully put together and all mercury manipulations involve danger. In this emergency I made the permissible supposition that for $P-p=0$, the value of η_4 is the same as that in Tables

97 to 99. This enabled me to reduce my relative data to the same standard as holds for the Tables 97 to 90. The diagram obtained fully corroborates all the inferences deduced. The obliquity of the lines decreases from low to high temperatures, *i. e.*, in proportion as the velocity of the axis flow decreases.

Apparent viscosity and temperature.—Considering these results as a whole, and representing the values of η when $P-p=0$ as a function of temperature, θ'', it appears that the curves lie farther away from the law $\eta''=\eta_0\,(1+\alpha\,\theta'')^{\frac{3}{4}}$ in proportion as R is larger. Thus the results, η, of Table 96, $R=0.008^{\text{cm}}$, conform very fully with this law; the results of Table 97, $R=0.018^{\text{cm}}$, fall considerably below it, and finally the results of Tables 98 to 100 where $R=0.025^{\text{cm}}$ lie in a very pronounced way below the former. As the bore is chosen larger, therefore, the effect of temperature becomes gradually less pronounced, and for $R=0.025^{\text{cm}}$ the law falls even as low as $\eta''=\eta_0\sqrt{1+\alpha\theta''}$. On the other hand, as the bore is chosen smaller the curves ultimately ($R=0.008^{\text{cm}}$) coalesce with the law, $\eta''=\eta_0\,(1+\alpha\theta'')^{\frac{3}{4}}$.

Obliquity of the linear loci.—In Table 104 I give a perspicuous view of the observed obliquity of the lines in Fig. 54, p. 304, φ being the angle of these lines with the horizontal relatively expressed. The temperature of transpiration being θ'', the value $\frac{\eta''}{\eta_0}$ in the table is computed from $\frac{\eta''}{\eta_0}=(1+\alpha\theta'')^{\frac{3}{4}}$. $\left[\frac{\eta''}{\eta}\right]$ however is computed from Fig. 54 when $P-p=0$.

TABLE 104.—*Transpiration of air in wide tubes.*

θ''	R	$\left[\frac{\eta''}{\eta_0}\right]$	tan ϕ	$\frac{\eta''}{\eta_0}$	$[\eta_0]\times 10^6$
0	0.008	1.00	20	1.00	240
977	(Table 96)	2.79	(00)	2.77	668
4	0.018	1.02	314	1.02	223
100	(Table 97)	1.10	298	1.23	244
625	....	2.14	64	2.23	474
1025	....	2.65	7	2.84	587
4	0.025	1.02	461	1.02	225
675	(Table 99)	1.81	228	2.30	404
865	....	2.06	166	2.60	458
1000	....	2.38	30	2.80	531
7	0.025	1.03	488	1.03	228
1050	(Table 100)	2.13	128	2.88	478
1280	....	2.50	44	3.20	560
*8	0.018	....	274	....	198
†8	(Table 108)	....	92	....	100
*7	0 012 (Table 107)	....	124	....	245

* Air. † Hydrogen.

For the given value of $\theta=4^\circ$ the values of the tan φ decrease about as rapidly as the square of R. It is to be noticed, however, that the tan φ in the case of Table 96 is probably zero, since the observed positive tan φ in Table 104 is compensated by an observed negative tan φ in other similar cases. Hence if tan φ is to be represented in its dependence both on η'' or θ and R, it will be necessary to assume an exponential form in which powers of both R and η'' are exponents.

Supplementary results.—To further elucidate the relations under discussion I made a series of miscellaneous low-temperature experiments. Table 105 contains data for a glass tube of fine but not rigorously uniform capillary bore. Here the variations of η with $P-p$ are quite insignificant, proving that the obliquity φ observed is not due to any imperfection of apparatus. The second part of the table contains results for a tube of larger bore than any of the metallic tubes. Nevertheless the variation of φ here is not proportionately large. The temperature of the receiver B, Fig. 44, is given under τ.

TABLE 105.—*Transpiration in glass tubes.*

[Capillary tube No. I. $L=30.0^{cm}$. $R=0.0117^{cm}$. $V=565.7^{cc}$. $\theta=6.6^\circ$.]

P	p	t''	$\frac{P^2-p^2}{p}\times t''$	$''$	τ	$\frac{\eta''}{1\times\frac{4\zeta''}{R''}}$
124.06	76.70	394	49040	6.6	21.0	0.0001505
123.96	76.70	398	49350	6.6	20.8	1515
88.91	76.63	1847	49220	6.6	21.2	1511
88.93	76.63	1838	49080	6.6	21.4	1508
124.08	76.50	394	49430	6.6	21.6	1517
124.06	76.50	394	49410	6.6	21.8	1518

[Capillary tube No. II. $L=34.25^{cm}$. $R=0.0302^{cm}$. $V=565.7^{cm}$. $\theta=6.6^\circ$.]

86.96	76.48	72	1613	6.6	21.7	0.0001946
86.89	76.48	73	1624	6.6	22.3	1960
85.66	76.48	82	1597	6.0	22.5	1933
85.72	76.48	82	1598	6.6	22.7	1935

Table 106 shows that similar variations of η with $P-p$ (i. e., the obliquity φ) occurs in case of silver tubes, the capillary being employed in two different lengths. Curiously enough, the value of φ here does not vary with L. There may, however, be a compensation in R. Silver capillary tubes could not be obtained in such excellent quality as the platinum tubes.

TABLE 106.—*Transpiration in silver tubes.*

[Silver capillary tube No. I. $L=71.00^{cm}$. $R=0.0181^{cm}$. $V=500^{cc}$. $\theta=6.7^{\circ}$.]

P	p	t''	$\frac{P^2-p^2}{p}\times t_{,,}$	θ''	τ	$\frac{\eta''}{1+\frac{4\zeta''}{R''}}$
				°		
122.61	75.85	281	34370	6.7	22.7	0.0002612
122.61	75.85	282	34490	6.7	22.7	2620
88.07	75.85	986	26040	6.7	22.7	1978
87.98	75.85	992	26010	6.7	22.9	1976
87.93	75.85	992	25880	6.7	23.0	1969
122.46	75.85	280	34120	6.7	23.1	2599

[Same spiral shortened. $L=35.27^{cm}$.]

119.59	75.90	158	17220	6.7	22.2	0.0002629
119.56	75.90	154	17310	6.7	22.0	2631
87.86	75.90	520	12820	6.7	21.8	1956
87.44	75.90	521	12940	6.7	21.6	1971
119.46	75.90	155	17380	6.7	21.2	2645

Table 107, with results for a fine platinum capillary, has been incorporated here, and corroborates the present results.

TABLE 107.—*Transpiration in platinum tubes. Air.*

[Capillary tube No. 9. $L=21.2^{cm}$. $R=0.0118^{cm}$. $V=565.7^{cc}$. $\theta=7.0^{\circ}$.]

P	p	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	τ	$\frac{\eta''}{1+\frac{4\zeta''}{R''}}$
				°		
*123.66	47.74	531	66640	7.0	19.0	0.0003049
123.80	47.88	530	66740	7.0	19.5	3060
88.17	12.25	2137	56570	7.0	20.1	2601
88.05	12.13	2163	56660	7.0	20.6	2607
83.30	12.38	2112	56540	7.0	21.2	2609
†123.63	47.74	525	65900	7.0	22.4	3053

* $p=75.92$. † $p=75.89$.

Table 108, with which I will close the present series of supplementary data, has a direct and important bearing on the discussion. Hydrogen and air are here passed through the same platinum tube consecutively.

TABLE 108.—*Transpiration in platinum tubes. Hydrogen.*

[Capillary tube No. 8. $L=40.5^{cm}$. $R=0.0182^{cm}$. $V=565.7^{cc}$. $\theta=7.8^{\circ}$. $p=74.95^{cm}$.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	τ	$\frac{\eta''}{1+4\zeta''/R''}$
112.56	37.59	107	10060	° 7.8	22.6	0.0001354
112.52	87.55	107	10050	7.8	22.7	1355
112.06	87.09	108	9990	7.8	22.8	1347
85.75	10.78	352	8160	7.8	22.9	1100
85.72	10.75	354	8160	7.8	23.1	1101
85.64	10.67	355	8120	7.8	23.2	1096
112.72	37.75	107	10110	7.8	23.3	1365
112.67	37.70	107	10090	7.8	23.4	1365

[Same apparatus with air.]

P	$P-p$	t''	$\frac{P^2-p^2}{p}\times t''$	θ''	τ	$\frac{\eta''}{1+4\zeta''/R''}$
120.47	45.55	202	24000	7.8	23.4	0.0003240
120.55	45.63	201	23930	7.8	23.5	3235
86.66	11.74	676	17120	7.8	23.2	2311
86.59	11.67	675	16980	7.8	23.0	2292
120.52	45.60	202	24030	7.8	22.8	3238

The results are very instructive. In the experiments (Fig. 54, p. 304) tan φ increases with the rate of flow, or, cæteris paribus, with the viscosity of the gas. Hence one would infer that in the case of hydrogen and air passing through the same tube, cæteris paribus, the obliquity would be decidedly greater. The experiment shows precisely the reverse result; tan φ diminishes more than proportionally to the viscosity the ratio (Table 104) being as 3 : 2.

General remarks.—I regret that my research must be closed with these experiments, and that it is not expedient to continue the work further. To do this I should need to repeat the work with special care in the measurement of temperature and in the determination of the capillary radius. Nevertheless, the survey of the present field of inquiry is by no means unsatisfactory. My results show conclusively that the character of the internal surface of the transpiration tube is of marked influence on the result. The absence of obliquity (φ) in glass, and its frequent occurrence in metallic tubes, may be referred to the smoothness and roughness of the respective internal surfaces. Rough surfaces are associated with eddies along the line of flow, by which it is retarded and apparent viscosity is increased. The absolute value of viscosity measured by transpiration through metallic tubes is greater than the viscosity measured by transpiration through glass tubes. This I have in general found, and although the effect of the discrepancy, possibly due to roughness, is not vital in case of my smallest tube, No. 10 (Tables 81 to 90, $R=0.008^{cm}$), I have none the less thought it wise to state my result, $\eta''=\eta_0(1+\alpha\,\theta'')^{\frac{2}{3}}$, with caution, and to pursue the present critical inquiry as far as the present section indicates. Inasmuch as I have proved that as R decreases from my largest to my smallest radius, the value of $F(\theta'')$, which holds for $P-p=0$, increases and finally merges into $(1+\alpha\theta'')^{\frac{2}{3}}$ independently of pressure, I have accomplished the main purposes of this section.

Intimately connected with the present discussion is the occurrence of surface condensation of gases on platinum. If the law of inverse squares holds, then there will be no tendency of gases to condense in the capillary canal, however finitely small. This follows from the constant potential of a homogeneous elliptical shell (of which the capillary tube may in a special sense be said to be compounded) on any points inclosed within it. But in the case of the law of inverse squares or any higher law, there may be condensation infinitely near the surfaces, together with the possibility that molecules condensed on the walls of the tube may again find their way into the canal. The occurrence of molecular aggregates in the canal or transpiring current of gas in virtue of surface action of the platinum can not therefore be assumed to be nil. [Kayser[1] finds that the height of the condensation atmosphere of ammonia on glass may exceed $.0002^{cm}$. Compared with the radius of my capillary tubes ($R=.008^{cm}$), this is by no means small. Hence there is reason to infer that the increased molecular aggregation of the transpiring gas is not negligible. In conformity with the results of Kayser and of Chappuis[2], O. Schumann[3] altogether rejects the transpiration method. I believe these strictures much too severe. Schumann's own observations are made at temperatures not exceeding 100°. Neither from these nor from any other earlier researches can the transpiration behavior of a gas between 400° and white heat be safely predicted. In tables 81 to 88 I have given the data in detail in order to show the excellent accordance of the data among themselves, even if an hour or more of heating to redness intervenes. The differences are clearly errors of observation. If, therefore, condensation discrepancies are present, their time of variation must be almost instantaneous.

Furthermore, the identity of law $(1+\alpha\theta)^{\frac{2}{3}}$ for both air and hydrogen is most easily interpreted as an immediate fact. Otherwise it will be necessary to suppose that air and hydrogen as regards condensation on platinum behave identically; or that possible differences of the law for air and hydrogen are just compensated by the condensation discrepancy. Both of these alternative hypotheses are exceedingly improbable. Again, the law $(1+\alpha\theta)^{\frac{2}{3}}$ applies for hydrogen at all temperatures between zero and white heat. It is therefore clear that in case of marked condensation the simple law in question would have to be replaced by a much more complicated function. If, finally, the transpi-

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[1] Kayser: Wied. Ann., vol. 14, 1881, p. 450.

[2] Chappnis: Wied. Ann., vol. 8, 1879, p. 1. Cf. J. W. Langley: Zeitschr, f. Phys. Chem., vol. 2, 1888, p. 83.

[3] O. Schumann: Wied. Ann., vol. 33, 1884, pp. 381, 385.

ration method were to be rejected, it seems to me that very little experimental elucidation of the thermal variation of gaseous viscocity will be obtainable. 1889.]

Again, the quantity actually measured is not η but $\frac{\eta}{1+\frac{\zeta}{4R}}$, where ζ is the coefficient of slip (Gleitungs coefficient); ζ being inversely proportional to pressure[1], or according to Meyer[2] and others, a direct expression for mean free path. Hence it must have a smaller value in the case of platinum tubes than in the case of tubes of glass, because of the tendency of gas to condense on metallic (platinum) surfaces. Whatever discrepancy is introduced by ζ will therefore be more serious in case of glass than in case of platinum. From this point of view results with metallic capillary tubes have greater claims to correctness. Further remarks on this quantity ζ I have given elsewhere.[3]

THE NEW METHOD OF PYROMETRY.

PRACTICAL REMARKS.

Appurtenances.—Having endeavored to investigate the theory of the transpiration thermometer it will be expedient to close this chapter with a few practical remarks. Equation 12, on page 281, shows that thermal data can be measured in terms of time, t, or of volume, V_0, or again in terms of the rate at which volume increases, $\frac{V_0}{t}$; or even in terms of the pressure factor, $\frac{P-p}{p}$. Any of these quantities varies as the $\frac{5}{3}$ power of absolute temperature, and hence the sensitiveness of the method. As regards expedition, however, the differential methods are possibly more serviceable; and either the volume method which I employ on page 293 or Mr. Holman's method used either with compression or exhaustion is available. Again, if a suitable jet-pump is not at hand and if the mercury apparatus, page 243, Fig. 43, presents too much practical inconvienence, a bell-jar arrangement, like the gasometer, Fig. 35*a*, page 179, in which the light bell may be weighted either positively or negatively, suggests itself. Such an apparatus may of course be made small and refilled for each measurement. Differential apparatus obviate the use of chronometers and of pressure measurements, and solution and other errors are similarly eliminated.

The transpiration pyrometer.—To fully utilize the accuracy of measurement of which the transpiration pyrometer is capable, it is necessary to give the instrument a different form from that used in the present pioneering experiments. Inasmuch as it was my object to study effects in-

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[1] Kundt u. Warburg: Pogg. Ann., vol. 155, 1875, pp. 337, 525.

[2] Meyer: Kinetische Theorie d. Gase, p. 152.

Barus: Wied. Ann., vol. 36, 1889, p. 383.

volving changes of the capillary bore of the tubes, no fixed or elaborate form of transpiration pyrometer would have served as well as the improvised arrangement described in Figs. 45 and 46. Equation 12, however, contains the clue for the construction of a practical transpiration pyrometer. The equation shows that the correction for ends decreases with extreme rapidity with the ratio of bores of the cold and hot parts of the pyrometer, i. e., as the fourth power of R''_0/R_0. Hence the distorting effect of cold ends can be easily eliminated by making the central parts of the tube slightly more capillary than the terminal parts. The accompanying diagrams suggest some serviceable methods by which this may be done.

Fig. 49 represents an available form of apparatus in which the terminal tubes *a* and *b* are relatively large, each of semicircular section with their flat sides juxtaposed. The capillary tube is shown at *c c*, and may be wound in any desirable spiral form, open or closed. To protect it an envelope *d* of platinum surrounds the helix of capillary tube *c c*., With regard to this form, it is to be noticed that the interior volume in the terminal tubes *a* and *b* must be reduced as far as possible so that thermal changes of the air inclosed may not sensibly affect the result. In view of the difficulty of welding the capillary tube *c c* into the larger terminal *a* and *b*, the form Fig. 50 has advantages. Here the terminal *a* is a circular tube, and is *drawn down* upon the capillary tube *c* by aid of the wire plate. By this method a tight joint may be produced in such a way as not to endanger the platinum capillary. Slight changes of the

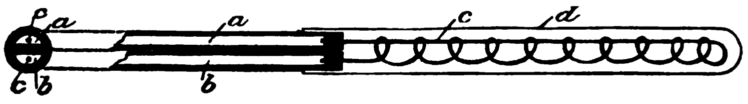

FIG. 49.

FIG. 50.

FIG. 51.

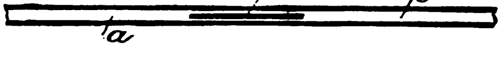

FIG. 52.

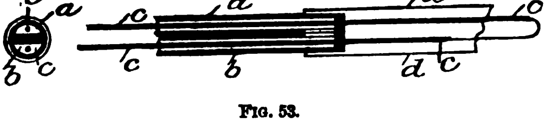

FIG. 53.

FIGS. 49, 50, 51, 52, 53, Diagrams of practical traspiration pyrometers.

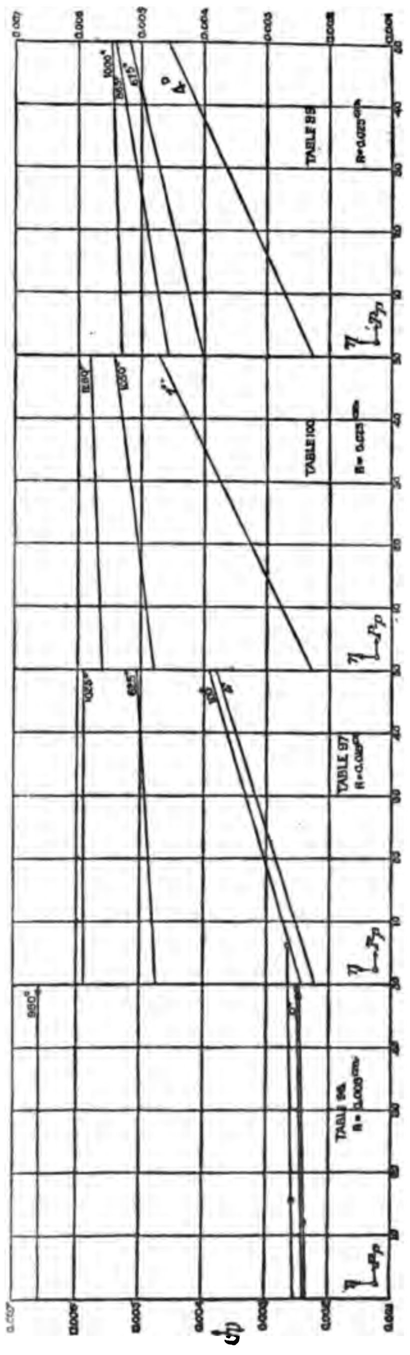

Fig. 54. Chart showing the relation between apparent viscosity and pressure.

capillary bore for the *small* length *d*, where the two tubes are in contact, will only change the mean radius R_0, and will be fully allowed for in measuring $\frac{R_0}{\eta_0}$ in the manner indicated. (See p. 282.)

Another way of making capillary tubes with large terminal ends is shown in the exaggerated diagrams Figs. 51 and 52. In Fig. 51 a smaller capillary tube is inserted at *c* in the larger tube *a b*. The latter is then drawn down in the wire plate until *c* has the requisite small diameter. Again, a simple platinum wire *c* may be inserted into the tube *a b*, as Fig. 52 suggests. These forms have the advantage as consisting of uniform tubes without soldering, so that the danger of leaks where the terminals join the tube is obviated.

Finally, the simplest and surest method of decreasing the central capillary bore consists in rolling down the central part in a wire-rolling mill, the two rollers of such a mill being appropriately grooved.

Without passing judgment on any of these forms, it is clear that the simple capillary tube used in the above experiments can be made to subserve the purposes of thermal measurement in the way shown in Fig. 53. Here the ends *c′ c′* of the platinum capillary tube *c′ c c c′* are surrounded by the larger tubes *a b*, and a current of cold water circulates with great rapidity from *a* into *b* across the septum. Knowing the temperature of the cold ends of the capillary (this being the temperature of the water in *a* and *b*), the correction member can be calculated. The tubes *a* and *b* are again made of semicircular section with their flat faces juxtaposed.

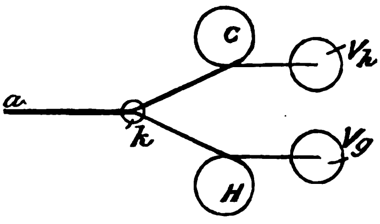

FIG. 55. Disposition of apparatus for differential measurement.

Returning from this digression to the typical form, Fig. 49, it appears that the practical dimensions given to the instrument need not exceed those of an ordinary mercurial thermometer. The capillary tube may easily be wound in a closed helicoidal form with an external diameter of not more than 0.6^{cm}, and a length not greater than 2.5^{cm}. Such a spiral can therefore be made to lie wholly within the central tube of my re-entrant porcelain air thermometer, Fig. 33, and the comparison between transpiration pyrometer and air thermometer may then be effected with nicety in the same way as has been explained above, page 180. It is merely necessary to replace the thermo-couple by the transpiration pyrometer in the diagram of the revolving muffle, to carry out the present comparison in detail.

Again, it is curious to note that by selecting capillary tube of small external diameter and keeping the terminals *a* and *b* insulated by plates of mica and the turns of platinum capillary tube apart (Fig. 49) the platinum spiral may be heated to any degree of redness by the current of a dynamo electric machine. To obtain extreme degrees of temperature it is of course necessary to surround the tube *c c* with some non-conducting substance, for instance layers of carded asbestos. If the free space surrounding the axis of the helix of platinum wire be large enough to admit the insulator of a thermo-couple snugly, a comparison between the indication of the transpiration pyrometer and of the thermo-couple may be made at once, the degree of high temperature being regulated by the electric current which circulates through the helix of the platinum capillary tube. This form of calibration apparatus appears to my mind to be at once the simplest and the most elegant as well as the most efficient form yet devised. Perhaps I may add that if the resistance of a hot platinum capillary tube be measured the thermal variation of resistance is obtainable for long ranges of temperature.

Supposing, therefore, that for a given (diatomic) gas the law of sixth roots characterizes the thermal variations of mean free path, it appears finally that the present method is especially well adapted for the high temperature study of dissociation phenomena in gases; for dissociation here means the degree of discrepancy between the law holding under the given condition of dissociation and the normal law of sixth roots. In the case where gases permeate platinum at high temperature (the case of hydrogen and of many hydrocarbon gases) it is necessary to inclose the transpiration pyrometer in a glazed porcelain tube which fits snugly around it. This tube is closed at the hot end, and filled with the hydrogen or other gas in question at a pressure equal to the mean pressure $\frac{1}{2}(P+p)$, at which transpiration takes place. In this way the occurrence of diffusion across the walls of the tube is obviated and the undistorted phenomenon is observable. Indeed, the envelope of porcelain tube to surround the platinum capillary apparatus is advisable in all cases where the pyrometer is directly exposed to flame or under other circumstances in which the permeation discrepancy is to be apprehended.

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